

INFORMATION DIVISION TRANSLATION 147-1

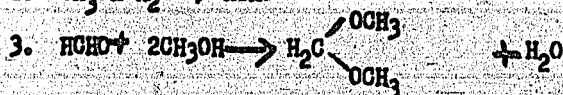
API-TOM Reel 3, Frames 220-226 incl.  
 Patent Application I.G. Farbenindustrie A.-G.  
 No. O.Z. 13545, Ludwigshafen a/Rh  
 July 9, 1942  
Process for Production of Ethylene Glycol

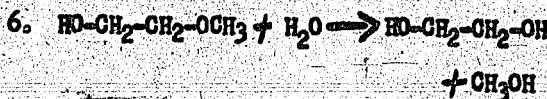
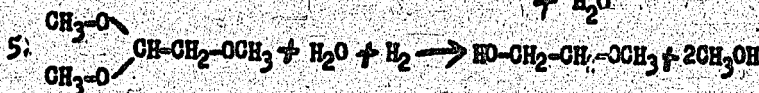
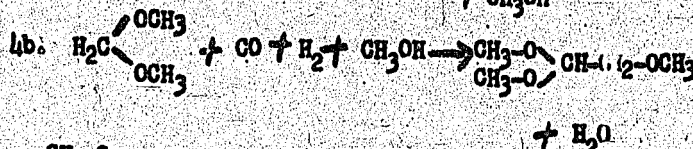
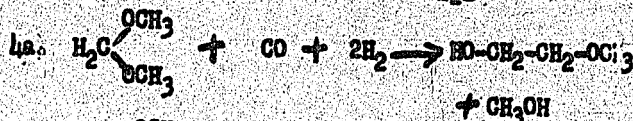
The processes known so far for the production of ethylene glycol used ethylene as a starting material, in which mostly ethylene chlorhydrin was produced by addition of hypochlorous acid, hydrochloric acid split therefrom, and the resulting ethylene oxide converted over to ethylene glycol. These processes have the disadvantage that they are bound to the existence of cheap electrical energy, since on ground of economy the hydrogen chloride resulting as a by-product in the form of its salts must be converted again into chlorine, which serves for production of the hypochlorous acid. Besides, ethylene is not very cheap and above all is not on hand in optional amounts as a raw material.

Its production from fermentation ethyl alcohol will always be dependent upon what amounts of fermentable carbohydrates important for human or animal nutrition stand available for this purpose. The production of ethylene by partial hydrogenation of carbide acetylene is once again connected with the existence of cheap electrical energy for the production of the necessary calcium carbide, and its recovery from waste gases, like coking gases, cracking gases, or hydrogenation gases, presupposes a highly developed coal refining industry.

A process for the production of ethylene glycol has now been found which, independent of ethylene and electrical energy, can be built up out of water gas, producible in the largest amounts from coal and water. It consists therein, that one converts formaldehyde with methanol to formaldehyde-dimethylacetal (methylal), this is converted, by means of treatment with a mixture of carbon monoxide and hydrogen in the presence of catalysts under increased pressure and at elevated temperatures, to a mixture consisting of oxygen-containing compounds, among others of ethylene glycol mono-methyl ether and methoxy-acetaldehyde-dimethyl acetal, and splitting the ethylene glycol monomethyl ether obtained from the mixture after a hydrolyzing hydrogenation.

The individual steps of the process can be represented somewhat by the following formulas:





The methanol necessary for starting material can be produced by known methods from CO and H<sub>2</sub> according to equation 1. Likewise the formaldehyde can be obtained from methanol in known manner by dehydrogenation according to equation 2. These dehydrogenations are suitably so carried out that immediately a mixture of methanol and formaldehyde results which is suitable for the further conversion. Formaldehyde dimethylacetal (Methylal) is produced according to equation 3 either by conducting a vaporized mixture of methanol and formaldehyde over catalysts, or better combination of both components in the liquid phase in the presence of suitable catalysts, for example sulfuric acid. The methanol necessary for the production of the acetal need not be especially pure, since impurities remain back in the distillation, on account of the low boiling point of acetal. The cheap crude methanol can be used with especial advantage, such as is obtained directly from the synthesis from CO and H<sub>2</sub>.

The conversion of formaldehyde-dimethylacetal to oxygen-containing compounds, preferably to ethylene glycol monomethyl ether, after equation 4a) and to methoxyacetaldehyde dimethylacetal after equation 4b) is done most suitably following the process of the patent (application I. 69,072 IVd/120) by treatment with a mixture of CO and H<sub>2</sub> under pressure and at elevated temperatures in the presence of catalysts, especially of metals which, like cobalt, are capable of forming carbonyls. By choice of proper conversion conditions, one obtains a mixture which is rich in components boiling at between 100-130°C, which mainly consists of the ethylene glycol monomethyl ether boiling at 122-124 and the methoxyacetaldehyde dimethylacetal boiling at 127-129°C. This is especially the case if one converted in the operation only a portion of the formaldehyde-dimethylacetal, that is, at times worked with an excess of acetal. Also elevation of the hydrogen partial pressure has the effect of formation of larger amounts of the desired low boiling product. Unconverted acetal is continuously recovered and conducted further to the reaction. Methanol present is separated and either used as such or partially or completely dehydrogenated to formaldehyde.

The mixture of oxygen-containing compounds obtained is then, (in emergency without separation of methanol), treated in an acid medium with hydrogen in the presence of hydrogenation catalysts, whereby the methoxy acetaldehyde dimethyl acetal and other acetals also, hydrolyze according to equation 5 to methoxy acetaldehyde and simultaneously are hydrogenated to ethylene glycolmonomethylether. It is possible to proceed by allowing a mixture, thinned with water and treated with some acetic acid, to trickle at a pressure of 100-300 atmospheres absolute and a temperature of 150-250° over a solid fixed hydrogenation catalyst, for example nickel or copper on silica gel, or one can stir or circulate the mixture treated with the finely-divided catalyst in the presence of hydrogen at 150-250° for so long until no more hydrogen is taken up. The mixture hydrogenated under these saponifying conditions is split up by distillation. The methanol on account of its particular purity is preferably used for the production for formaldehyde, and lead back into the cycle. The ethylene glycolmonomethylether is partly recovered as an azeotropic mixture with water, partly as a pure compound of boiling point 122-124°C. The high-boiling portions can be used as such or split up into fractions for desired purposes. They are odorless, very viscous, and miscible with water in all proportions. They can find use as such or after further transformation, for example, esterification, as glycerine substitutes, softeners, thickeners or equalizers.

The splitting of ethyleneglycolmonomethylether according to equation 6 occurs advantageously by heating the aqueous solution to high temperatures, for example, at 200-330°C, in the presence of small amounts of acid catalysts, for example mineral acids like phosphoric acid, or acid salts, like acid phosphates, or also organic acids like acetic acid. One can undertake the splitting of the ether in interrupted operating method in pressure vessels or also can carry it out continuously, somewhat in the manner that one conducts the aqueous solution of the ether mixed with the catalyst through heated tubes, and thereby suitably chooses the retention time in the hot zone so that by each pass only a portion of the ether is split to methanol and ethylene glycol. With more severe conditions, perchance at higher temperatures, or with longer retention time of the reaction mixture at the splitting temperature, or also by addition of larger amounts of acid medium, smaller or larger amounts of acetaldehyde result, which may be recovered and used. The separation of the resulting mixture of methanol, ethylene glycol and water is accomplished by distillation. The methanol can, however, be distilled out even during the splitting. The azeotropic mixture of ethylene glycol and water obtained in small amounts from the distillation of the aqueous solution of ethylene glycol can suitably be returned to the splitting without further separation, while the pure ethylene glycol is recovered as such.

#### EXAMPLE

One allows a mixture of methanol and formaldehyde of the composition 3:1, which is produced by the incomplete catalytic oxidation of methanol with air, and with which about 0.5% sulfuric acid is mixed, to flow through four heatable vessels connected in series, provided with

fractionating columns, with an hourly quantity which corresponds to about the half of the total contents of the usable volume of the four containers. The transition temperature at the head of the column is held at  $42^{\circ}\text{C}$ , while the bottom temperature in the substance in the individual stills, as the acetal formation progresses in the flowing-through of the mixture through the vessels, rises from  $55$  to  $80^{\circ}$  in the direction of throughput. The mixture released from the fourth still contains practically no more formaldehyde. Excess unconsumed methanol is recovered continuously and conducted back to the working process. An azeotropic-boiling mixture of 92% methylal and 8% methanol is obtained with practically the calculated yield.

In a pressure vessel of 50 liters contents are stirred 25 kg. of a mixture so-produced of methylal and methanol after addition of some 1% of a ground catalyst containing 20% cobalt on silica gel, with a carbon monoxide-hydrogen mixture 1:2 at 200 atm. for so long until some 40% of the methylal is converted. The resulting mixture is fractionally distilled after separation of the catalyst. Besides 15 kg. of unconverted 92% methylal and some 3 kg. methanol, 8.7 kg. of reaction product are obtained, of which 70% boils from  $100$  to  $130^{\circ}$ , and which consists of about equal parts of glycolmonomethylether (b.p.  $122-124^{\circ}$ ) and methoxyacetaldehyde dimethylacetal (b.p.  $127-129^{\circ}$ ), as well as small amounts of water. The residual 30% boils between  $80$  and  $150^{\circ}$  at a pressure of 10 mm. Hg.

The resulting 8.7 kg. of reaction product is then diluted with the same amount of water and stirred in a pressure vessel, after addition of 0.3% acetic acid and 400 g. ground nickel-containing silica gel, at  $220^{\circ}$  under a hydrogen pressure of 200 atm. for so long until no more hydrogen is taken up. After separation of the catalyst, it is fractionally distilled. In addition to 2.9 kg. methanol and 1.6 kg. glycol ethers boiling between  $150$  and  $270^{\circ}\text{C}$ , there is obtained 3.7 kg. glycol monomethyl ether in the form of a mixture with water boiling at  $100^{\circ}\text{C}$ , which after addition of 0.5% phosphoric acid, is then heated in a closed vessel for an hour at some  $250^{\circ}$ . From the distillation of the mixture obtained there is recovered, besides small amounts of acetaldehyde, 390 g. methanol and 75% of the introduced glycol monomethylether as an azeotropic mixture with water. 630 grams ethylene glycol of boiling point  $197-198^{\circ}$  remain as residue, corresponding to a yield of 90% of that calculated, referred to glycolmonomethylether split.

#### PATENT CLAIM

Process for the production of ethylene glycol, characterized thereby, that formaldehyde reacts with methanol to formaldehyddimethylacetal, this converted catalytically under pressure and at elevated temperature with carbonmonoxide and hydrogen to oxygen-containing compounds consisting among others of ethylene glycolmonomethylether and methoxy aldehyde dimethylacetal, and to split the ethylglycolmonomethyl ether obtained after a hydrogenating saponification to ethylene glycol.

I.G. Farbenindustrie Aktiengesellschaft

Requested by B.H. Shoemaker

Translated by G.C. Miller - Jan. 7-8, 1947

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-6

API-TOM Reel 6, Frames 263-

Patent Application O.Z. 12,438

B 190 197 IV d/120, presented March 18, 1940

Process for the Separation of Aliphatic Oxygen-Containing Compounds

as well as Straight Chain Hydrocarbons with at Least Six Carbon Atoms from Mixtures Including Such.

The process rests on the knowledge that aliphatic oxygen-containing compounds, just as hydrocarbons with straight, unbranched chains, unite with urea easily and quickly to well-defined, good crystallizing addition compounds, while hydrocarbons with branched chains act indifferently in this respect. Preliminary condition is a certain minimum length of the carbon chain. The lower limit is at 6 C-atoms.

The addition compounds thus obtained are decomposed into the components by heating or addition of urea looseners (decomposing agents) such as example methanol and other low aliphatic alcohols, better yet by water or water-containing solutions. In general one obtains in the latter-named method without further ado a stratification into, for example, a water solution containing urea and above it the pure oxygen-containing compound or hydrocarbon separates.

On this knowledge rests now the following invention. It consists therein, that one can separate aliphatic oxygen-containing compounds or straight chain hydrocarbons from such containing mixture, in that one reacts this mixture with urea, the hereby-formed addition compounds separated by decanting, filtration or similar method, and then decomposed by heating or addition of urea solvents into the components.

Oxygen-containing compounds which can be separated from the mixture according to the invention are, for example:

octanol primary and secondary  
cetyl alcohol  
n-decyl alcohol

heptaldehyde  
nonaldehyde  
decylaldehyde  
undecylaldehyde

methyl nonyl ketone  
methyl undecylketone

caproic acid  
caprylic acid  
undecylenic acid  
oleic acid  
palmitic acid  
stearic acid

pelargonic ester  
enanthoic ester

In order to carry out the previous process one can, for example, bring together the optional mixture which contains the named materials with a concentrated solution of urea in water, methanol or ethanol and the like. Thereupon, advantageously after good mixing, the solid crystalline addition compound of the named substance separates. It is separated and by addition of water or, at pleasure, aqueous solutions decomposed into the components.

In this manner, the higher, as they come from the catalytic preparation process or fermentation process as a crude mixture, can be isolated in pure form or, if necessary, further worked up by rectification.

Furthermore, the process is suitable for the decomposition of ethereal oils. So from the oil of rue methyl-nonylketone can be separated.

In the case of these compounds of urea with higher alcohols, aldehydes, ketones, acid and esters separated according to the process at hand, they act probably like molecular compounds. In any case, the analysis in most instances has shown that the compound consists of a complex of 6 urea molecules and one molecule of the other component.

The formation of these compounds one can in many cases control with the smallest amounts under a microscope. If one places in a concave slide a drop of octanol and then adds to it a few small crystals of urea, so one sees after a few moments long fine needles shoot out between the proportionately stout urea crystals. After several minutes the urea crystals are filled with countless fine needles, so that they give the appearance of magnetic bar overgrown with iron filings. The formation of these addition compounds proceeds with different substances at different speeds. The speed is so great with the esters used by us that one must take pains to bring the preparation rapidly enough under the microscope in unaltered condition. They are completely overgrown within a moment. Not less stimulating is it also to stratify carefully a concentrated alcoholic urea solution with a trace of the aforementioned material, for example, pelargonic ester and to observe how the long fine needles of the addition product shoot out at the contact surface.

A further important form of carrying out the applied invention consists therein, that one can decompose, accordingly, a hydrocarbon mixture which contains compounds with straight and with branched chains into these two components. Fundamentally this decomposition is of unusual technical interest because the hydrocarbons with branched chains produce, by virtue of their knock resistance, ideal propellant for carburetor engines, as for example, airplane engines.

Also for the working up of lubricants the process is of significance, especially the components with straight chains possess, in general, especially favorable technical lubricating properties. According to the invention one can work up in the mentioned manner hydrocarbon mixtures of various types or fractions thereof. As starting materials are named for example: mineral oil or fractions thereof, i.e., naphtha, petroleum, gas oil, diesel oil, paraffin oil, vaseline. Furthermore, hydrocarbon mixtures formed in the dry distillation of lignite or mineral coal. Besides then, products of the destructive hydrogenation of lignite, mineral oils, tars, further polymerization naphtha, cracked bensins and others.

In order to work up these materials according to the aforementioned process, one can, for example, combine the above with a saturated solution of urea in methanol. Thereupon, the compounds with straight chains precipitate in the form of their urea-addition compounds and can be set free therefrom by decomposition with heat or addition of small amounts of water. Those remaining which were unaffected by urea, essentially compounds of branched chain hydrocarbons, can be used directly after the separation as high-grade strong knock resistant motor fuel (aviation bensins).

Further experiments have shown that the amount of the solvent can be reduced considerably. One needs only to add sufficient solvent so that the urea is well impregnated with it. The process proceeds so that a small part of the urea goes into solution at a time and immediately separates in the form of the addition compound, so that new urea can dissolve and enter into reaction. The solvent acts thus as a catalyzer to a certain degree.

#### Example 1

50 g. of oil of rue were vigorously shaken with 500 cc. of a saturated aqueous or alcoholic solution of urea. The crystalline paste which separates immediately is filtered with suction and decomposed by shaking with 200 cc. water. Thereupon the methyl-nonyl ketone separates on the aqueous urea solution.

#### Example 2

A cold saturated solution of urea in methanol or ethanol, immediately yields with a drop of n-octane but not with isooctane, on shaking, a crystalline separation of the addition compound. If one thereupon reduces the concentration of the urea, the compound decomposes into its constituents. It is therefore, as all such compounds prepared in the manner of the invention, stable only in an "urea-atmosphere". With water it decomposes spontaneously with separation of the unchanged n-octane. It is dissociated also by dry heat with separation of the n-octane.

Example 3

Petroleum or naphtha is shaken with an excess of urea in a methanolic or ethanolic solution. The separated addition compound is filtered by suction and decomposed by heating or addition of alcohol or water for the separation of the normal hydrocarbon. From the filtrate the hydrocarbons with branched chains were separated, if necessary, after the removal of the major portion of solvent, by addition of water.

Example 4

100 cc. of test naphtha (150-180°C) was vigorously whipped up with 40 cc. of urea for its part well wetted by ca. 35 cc. methanol. After a short time the separation of the addition compound is completed. This is, as given in Example 3, filtered and decomposed. There is obtained in this manner ca. 40% normal and ca. 60% iso-hydrocarbons.

Example 5

300 cc. paraffin oil was vigorously shaken or agitated by a stirrer with 150 cc. of an alcoholic urea solution. The separated crystals were washed with a fat solvent. It yields then on decomposition with water the normal hydrocarbons in the form of soft paraffin. The decomposition of these crystals by water is especially beautiful to observe. Under the microscope one sees how the small stout crystals on wetting by a trace of water fly apart with violent motion, exploding to a certain degree, and in their place enter innumerable minute oil drops.

Example 6

The separation of the normal from the iso-hydrocarbons also succeeds with crude petroleum; here the process is especially advantageous. If one shakes crude petroleum with alcoholic urea solution, one obtains three different constituents. The normal hydrocarbons present separate as granular crystals, while it pulls with itself the tarry portions. One can separate the two, in that one filters vigorously, whereupon the tar goes into the filtrate with the solvent, and since it is insoluble in it can be skimmed off. Or: one filters only weakly so that only the alcoholic solution passes through, then changes the receiver and vigorously sucks off the tar. The last residues of the tar are removed by an appropriate solvent. From the first alcoholic filtrate are separated the iso-hydrocarbons in the manner described above. One has thus a resolution of the crude petroleum in three different groups of constituents, namely, (1) n-hydrocarbons, (2) tarry constituents and (3) iso-hydrocarbons.

This process need not be of advantage only in the refining but also for the scientific investigation of petroleum.



Patent Claims

1. A process for the separation of oxygen-containing aliphatic compounds or of straight chain hydrocarbons from mixtures containing such, thereby distinguished, that one adds urea to these mixtures, the compounds formed thereby separated by decanting, filtering or the like and separate finally the pure compounds from them by heating or addition of urea solvents.

2. Process according to claim 1 for the separation of alcohol, aldehydes, ketones, esters or acids of the fatty series with at least 6 carbon atoms, thereby distinguished, that one brings into reaction mixtures containing such with urea advantageously in the presence of limited amounts of urea solvents, such as water or the lower aliphatic alcohols, the addition compound obtained separated from the liquid and from it finally set free the named oxygen-containing compounds by further addition of urea solvent.

3. Process according to claim 1, thereby distinguished, that one brings into reaction mixtures, which contain straight chain hydrocarbons with at least 6 carbon atoms, and urea, advantageously in the presence of limited amounts of urea solvents, the solid separated portion removed from the liquid portion remaining and finally set free the straight chain hydrocarbon by heating or by addition of further amounts of a urea solvent.

4. Process according to claim 1 and 3, thereby distinguished, that one obtains hydrocarbon motor fuels by means of the urea compound decomposed into one part rich in the branched chains, i.e. knock resistant and other part rich in the straight chain hydrocarbons, for example, suitable as Diesel oil.

/s/ Dr. Bengen

Frankfurt-am-Main-Escherheim  
Mummstrasse 7

Translated Jan. 18 and 25, 1947 - H.G. Cohen  
Checked Jan. 29, 1947 - CCM  
Requested by R.F. Marschner

"Verfahren zur Abtrennung von aliphatischen sauerstoffhaltigen Verbindungen, sowie von geradkettigen Kohlenwasserstoffen mit mindestens 6 Kohlenstoffatomen aus solche enthaltenden Gemischen".  
Discoverer Dr. Friederich Bengen  
Frankfurt am Main  
8 pages, no illust.

S. O. C.  
Development (N. J.)

Translation of Technical Oil Mission Microfilm Reel 7  
Bag 2746, Target No. 30/4.08  
Gelsenberg (Orig. Ident. Reel 7A)

From a report on analytical methods of charge, intermediates, and end products of the high pressure hydrogenation plants at Ludwigshafen and Oppau.

#### ANALYSIS OF GASES

##### Sampling

Samples are collected either in flasks of 10 to 20 liter capacity or in gas holders or so-called "gas wursten" of different sizes (100 cc to 5 liters), depending on the kind of gas under investigation and on the kind of test. However, round flasks are also used.

A displacement fluid is necessary when using flasks or aspirators, while the "gaswurst" or round flask is evacuated beforehand, or is made air-free by flushing with the gas under investigation.

Activated carbon towers are also available which are "loaded" in the plant and degassed in the laboratory with super-heated steam.

##### Confining Fluids

Mercury, water, aqueous solutions, and in special cases organic solvents such as Glysantin (trade name?), are used as confining fluids. The following properties are required of a confining fluid:

1. It should not be too viscous, since otherwise it runs down the walls of the burette too slowly and makes the readings either inexact or too slow.
2. It should not dissolve any constituent of the gas under analysis.
3. It should not react chemically with the gas or any of its components, or catalyze their decomposition.

Mercury most completely fulfills conditions 1 and 2, but it is not useable with many gases on account of its reactivity with hydrogen sulfide, in addition to requiring very careful handling of glass vessels filled with it, on account of its high specific gravity. Since most gases containing hydrogen sulfide are freed of it by cobalt acetate before their further analysis, mercury is the best suited confining fluid for exact gas analysis and is so used at Ludwigshafen as well as at Oppau. Precautions against its toxicity are taken by means of special ventilation arrangements, especially with the Stock apparatus, where each mercury vessel is isolated from the atmosphere by means of a tube of activated carbon. Moreover a funnel-shaped movable suction appliance is placed over each mercury vessel.

Of all the gas constituents, ammonia and carbon dioxide show the greatest solubility in aqueous confining fluids. When using a wet test meter with gases containing ammonia, the ammonia must be removed by means of a sulfuric acid absorption flask ahead of the meter.

In regard to the solubility of carbon dioxide, it may be observed that:

1. The solubility of carbon dioxide in dilute HCl or  $H_2SO_4$  is just as great as in water.
2. The solubility of carbon dioxide decreases with increasing salt concentration, independently of the presence of acids.
3. The solubility of carbon dioxide in salt solutions even increases if very much HCl is present.

The commonly used water acidified with  $H_2SO_4$  to which an indicator is added gives no decrease in carbon dioxide absorption over pure distilled water.

Confining fluids with the least absorptivity for carbon dioxide are:

1. 20%  $Na_2SO_4$  solution with 5%  $H_2SO_4$ , which absorbs 0.26 volume percent of carbon dioxide.
2. A table salt solution consisting of 22 parts of NaCl in 78 parts of water. Acidification of this solution is purposeless.
3.  $MgCl_2$  solution.
4.  $CaCl_2$  solution - saturated.

This last solution absorbs extraordinarily little carbon dioxide but has a high viscosity and on this account is little suited for use as a confining fluid. Slight acidification of the confining fluid and addition of an indicator merely shows that the solution has not become alkaline.

A mixture of water and glycerine in a 1:1 ratio is sometimes used.

In the absence of hydrocarbons, aniline is well suited as a confining fluid (flat meniscus) since carbon dioxide and oxygen are little soluble in it.

### Simple Absorption Apparatus

The essentials of the absorption apparatus used at Ludwigshafen and Oppau are simple Hempel pipettes, whereby the gas comes in contact only with the surface of the absorption liquid and the small amount adhering to the walls of the vessel. Since the absorption is thus generally very slow, many passes of the gas to the absorption pipette are necessary before the reading finally becomes constant.

The newer absorption vessels, especially in combination with the Drehschmidt "Ketten" burette, are the so-called "kleine" pipettes (Stahl and Eisen, 26, 1385 (1906)), in which the gas is led in through a sealed-in glass tube almost to the bottom of the vessel. A sealed-in glass valve prevents the liquid from back-flowing. Since the valve must be kept very clean, the pipette is not suited for absorption liquids with high salt content where precipitate or sediment can appear.

### Apparatus Assemblies

Of apparatus assemblies which are useful in the plant as well as in the laboratory, the Orsat, holding up to 7 pipettes depending on the kind and composition of gas to be analyzed, may be mentioned. Stationary forms of the Orsat apparatus are generally used.

The measuring burettes are water jacketed in order to hold the temperature constant. Generally they have a widened cylindrical portion in the middle or in the upper half, whereby the burette is shortened considerably without reducing the accuracy of the reading. With burettes of 500 and 1000 cc. volume, a parallel second burette with fine graduation from 0 to 20 cc. is connected (in each case with water jacket). This serves for determination of the residue gas after combustion, where the wide burette would be too inexact.

The combustion of hydrogen at 270-280° and of hydrocarbons at red heat (700-800) is always carried out over CuO in a quartz or NCT tube. Temperature is measured either with a thermometer at 270° or with thermoelement at both temperatures. A gas burner is used to heat the combustion tube.

For the separation of mixtures of gaseous hydrocarbons, an apparatus is used which works according to the principle of distillation: the Podbielniak column.

The gas mixture is slowly led through a gas washing bottle containing KOH to remove H<sub>2</sub>S and CO<sub>2</sub>, then through a U-tube containing CaCl<sub>2</sub> for drying, and finally the condensible portion is condensed in a vessel cooled with liquid nitrogen. The non-condensibles are taken off and analyzed in the normal way. The condensible portion is separated by fractional distillation and measured volumetrically.

A report has already been made on the use of the Podbielniak column for separation of liquid hydrocarbon mixtures. (S. )

The Stock apparatus may also be mentioned for the separation of gaseous hydrocarbons. This is used in Oppau (Dr. Hiecke). In contrast to the Podbielniak with fractional distillation, the Stock apparatus operates on the principle of fractional condensation.

#### Types of Analysis

##### 1. Absorption and Combustion Methods

###### a. Technical Gas Analysis

Technical gas analysis at Ludwigshafen is carried out according to the following scheme:

###### CO<sub>2</sub> Determination

100 ccs. of gas is measured in a Hempel burette, passed into a Hempel pipette containing 50% KOH solution, and after the resulting absorption of CO<sub>2</sub> the volume is again read. Volume decrease = % CO<sub>2</sub>

###### Determination of Unsaturated Hydrocarbons

The gas is led into a saturated bromine water pipette. After shaking at least 3 minutes the bromine vapor is absorbed in KOH. Volume decrease = % unsaturated hydrocarbons.

###### Oxygen Determination

For the determination of oxygen, the gas is led over phosphorus or alkaline pyrogallol (Pyrogallol solution: 25 gm. pyrogallol and 750 ccs. water are mixed. This solution is mixed just before use with the same quantity of KOH (1:1), e.g., 50 ccs. solution and 50 ccs. KOH (1:1). Volume decrease = % O<sub>2</sub>.

###### CO Determination

For absorption of CO, the gas is led into two pipettes filled with alkaline or hydrochloric acid solution of cuprous chloride; first to one that has already been used, then to fresh solution. Finally the HCl vapor is absorbed in KOH. Volume decrease = % CO.

Alkaline cuprous chloride solution: 250 gm. ammonium chloride is dissolved in 750 cc. of water, 200 gm. of cuprous chloride added and shaken in a closed flask. Finally there is added 300 ccs. of NH<sub>3</sub> (sp. gr. 0.910). One cc. solution absorbs 16 ccs. CO.

Alkaline cuprous chloride solution: 11-12 parts cuprous chloride, 13-14 parts ammonia, and 74-76 parts water. One cc. absorbs 31 ccs. CO.

**Hydrochloric acid cuprous chloride solution:** The bottom of a 2-liter flask is covered with a 1-cm. layer of cupric oxide, hydrochloric acid added (700 ccs. + 300 ccs. water) and a copper spiral reaching to the neck of the flask inserted. The solution should be used only when colorless.

#### H<sub>2</sub> Determination

The remaining gas residue is transferred to the proper apparatus (burette filled with saturated CaCl<sub>2</sub> solution, quartz combustion tube filled with copper oxide, a pipette filled with CaCl<sub>2</sub> solution, a third pipette filled either with phosphorus or alkaline pyrogallol solution). First the quartz tube is heated to 250-270° and the gas led back and forth through it until the volume is constant. The quartz tube is then cooled and the volume decrease (= % hydrogen) read.

#### Determination of Saturated Hydrocarbons and Average N

The quartz tube is heated to a red glow and the gas passed back and forth through it until constant volume is obtained. The tube is then cooled and the volume increase obtained.

The gas is then led over the red glowing copper oxide into the KOH pipette until the gas volume is constant, the quartz tube is cooled down and the volume decrease measured (= % saturated hydrocarbon). The residue of gas now remaining = % nitrogen.

For the analysis of a hydrocarbon content of 5-10%, 500 ccs. instead of 100 ccs. is taken. For analysis of up to 5% hydrocarbon, 1000 ccs. of gas is used.

If an exact average n value of the gas is required, an exact instead of technical analysis is performed, in which mercury is used as the confining fluid instead of calcium chloride solution.

Example - 100 ccs. gas taken:

1. Over KOH 0.8 cc. = 0.8% CO<sub>2</sub>
2. Over saturated bromine water 2.00 cc. = 1.2% C<sub>n</sub>H<sub>n</sub>  
followed by absorption in  
KOH
3. Over phosphorus or alk. 2.20 cc. = 0.20% O<sub>2</sub>  
pyrogallol
4. Over cuprous chloride solu- 2.80 cc. = 0.60% CO  
tion
5. Burned over CuO at 270-280° 73.00 cc. = 70.20%  
H<sub>2</sub>

6. Burned over CuO at red heat, confined by CaCl <sub>2</sub> solution	2.80 cc. = 70.20 cc. increase
7. At red heat confined over KOH	97.00 cc. = 24.00% hydrocarbon
8. Residue	3.00 cc. = $\frac{3.00\% \text{ N}_2}{100.00\%}$

Calculation of average n:

Increase + hydrocarbon divided by hydrocarbon = average n.

$$70.2 + 24.0 = 94.2 \div 24.0 = 3.93$$

$$\text{Average n} = 3.93$$

On the Absorption of Oxygen

A highly concentrated chromous chloride solution is by far the best absorbent for oxygen.

Granular metallic chromium (6 RM/kg) to the amount of 600 gms. is dissolved in 6 liters of concentrated HCl.

A 20% chromous chloride solution of pure blue color is obtained which can be used for gas analytical purposes without further treatment after decantation in the absence of air.

To regenerate the solution, add 200 cc. concentrated HCl to the used but undiluted solution, and subject it to electrolytic reduction in an electrolysis bath (40 hours at 8 amps. current intensity). After filtration through a sand filter the solution is treated in the stock bottle with H<sub>2</sub> for 2 hours at 90° in order to remove any impurities.

If fresh chromous chloride solution is to be prepared, 800 cc. of HCl and 250 cc. of a 50% chromic acid solution is added to 3 liters of regenerated chromous salt solution and the resulting chromous chloride solution reduced as above. In this case, blowing the solution with hydrogen is not necessary. By boiling the solution can be concentrated unobjectionably.

The reaction between acid or neutral solutions of chromous chloride or chromous sulfate and oxygen proceeds quantitatively. Acid solutions of chromous chloride develop small quantities of hydrogen. The solubility of Cr II salt causes slight error. With consideration of these small corrections, the accuracy of the analysis of oxygen-nitrogen mixtures amounts to 0.04%.

Journ. Res. Nat. Bur. Stand. 1938, Vol. 21, p. 45.  
Chemiker-Zeitung, 63, 3/41939.

**b. Precise Gas Analysis**

Precise gas analysis is carried out at Ludwigshafen with the Orsat apparatus furnished by the firm of E. Haage, Mülheim/Ruhr.

The apparatus consists of a metal frame with two measuring burettes, several absorption pipettes (according to Dr. Tramm), and a combustion tube (20 cm.) of NCT material. A conventional Schnitt burner is used for heating.

**Absorption Pipette Solutions:**

- 1st Pipette: 30% KOH for absorption of CO<sub>2</sub>. One cc. KOH absorbs 40 ccs. CO<sub>2</sub>.
- 2nd Pipette, for butylene (C<sub>4</sub>H<sub>8</sub>): 75% H<sub>2</sub>SO<sub>4</sub> - a very temperature sensitive reaction since propylene is absorbed concurrently.
- 3rd Pipette, for propylene (C<sub>3</sub>H<sub>6</sub>): 87% H<sub>2</sub>SO<sub>4</sub>. An interpolation correction is necessary since ethylene is also absorbed concurrently.
- 4th Pipette, for ethylene (C<sub>2</sub>H<sub>4</sub>): Silver sulfate-sulfuric acid, prepared as follows: 5 gms. AgNO<sub>3</sub> is covered with concentrated sulfuric acid and evaporated until the disappearance of nitrous fumes, then diluted to 250 ccs. with concentrated H<sub>2</sub>SO<sub>4</sub>. Carbon monoxide is absorbed from gases containing more than 6% CO.
- 5th Pipette, for heavy hydrocarbons (C<sub>n</sub>H<sub>n</sub>): Fuming H<sub>2</sub>SO<sub>4</sub>, containing about 25% SO<sub>3</sub>.
- 6th Pipette, for oxygen: Alkaline pyrogallol, prepared by mixing one part of 40-50% pyrogallol solution with two parts concentrated KOH. One cc. of this solution absorbs 12 ccs. oxygen.
- 7th Pipette, for carbon monoxide: Ammoniacal cuprous chloride. 200 gms. CuCl is shaken with 250 gms. NH<sub>4</sub>OH and 750 ccs. H<sub>2</sub>O in a closed flask. To 3 volumes of this solution add 1 volume of concentrated ammonia (sp.gr. 0.910). Store over metallic copper. One cc. of this solution absorbs 16 ccs. CO. Since the absorption of CO is not complete and occurs only very slowly, 2 cuprous chloride pipettes are used. The last of the CO is then removed in the 8th pipette.
- 8th Pipette, for carbon monoxide: beta-naphthol. Ten gms. of copper oxide is made into a paste with water. Part of 250 ccs. of concentrated H<sub>2</sub>SO<sub>4</sub> is added, then



20 gms. of beta-naphthal, and finally the remainder of the  $H_2SO_4$ . In case the solution proves to be too thick, it is diluted with concentrated  $H_2SO_4$ . This reagent has a limited life, but absorbs CO rapidly.

9th Pipette, for butane ( $C_4H_{10}$ ) and propane ( $C_3H_8$ ). In the preparation of this reagent, 10 gms. of finely pulverized iodine pentoxide is well ground in a mortar with part of 125 gms. of 2.5% fuming  $H_2SO_4$  (46 gms. 96%  $H_2SO_4$  and 54 gms. of 20% fuming  $H_2SO_4$  per 100 gms. of solution), the rest of the acid is added and the mixture well shaken for 1 hour. The pipette should be filled with the mixture only shortly before the analysis and must be withdrawn through an attached stopcock immediately after the analysis. The mixture must be shaken again before each analysis.

Combustion Tube Packing:

Copper oxide in wire form in a temperature-resistant, nickel-chrome tube is used for the combustion of hydrogen and methane. It is heated to  $270-280^\circ$  as is usual for the combustion of hydrogen. For the combustion of hydrocarbons it is heated to a red glow.

If propylene and butylene are to be determined, the butylene is first absorbed in 75%  $H_2SO_4$ ; on the other hand, if the unsaturated and heavy hydrocarbons are to be determined in toto, they are absorbed in fuming  $H_2SO_4$ , and the  $SO_3$  fumes then removed by KOH.

In the separation of unsaturated hydrocarbons, readings must be taken after each pass. After reaching a constant volume decrease per pass the gas is passed to the next pipette. By no means can a constant volume be attained. For instance, with the following values:

	75% $H_2SO_4$		87% $H_2SO_4$		Ag- $H_2SO_4$
	25.1		32.4		40.2
(1)	28.0	(1)	35.9	(1)	40.7
(2)	29.0	(2)	37.6	(2)	40.8
(3)	30.9	(3)	39.0	(3)	40.9
(4)	31.4 0.5	(4)	40.0	(4)	41.0
(5)	31.9 0.5	(5)	40.2 0.2	(5)	41.0
(6)	32.4 0.5	(6)	40.4 0.2		
		(7)	40.6 0.2		

one obtains for butylene  $0.5 \times 6 = 3.0$ ;  $32.4 - 3.0 = 29.4$ , and thus the difference  $29.4 - 25.1 = 4.3\%$  butylene in the gas.

For propylene there is analogously obtained:  $0.2 \times 7 = 1.4$ ;  $40.2 - 1.4 = 38.8$ ; here the 3.0 ccs. of propylene absorbed in the 75%  $H_2SO_4$  must be added, giving

$$38.8 - 32.4 + 3.0 = 9.4\% \text{ C}_2\text{H}_6$$

If there is much CO in the gas the value for ethylene must be similarly interpolated.

The absorption of O<sub>2</sub> follows in known manner. After the absorption of CO, first in cuprous chloride solution and then in beta-naphthol, the combustion of H<sub>2</sub> is carried out at 270-280° over CuO. After cooling and reading, the combustion of hydrocarbon follows. Sudden cooling must be avoided here, else oxygen is given off by the CuO.

Example:

	Reading, cc.	% Content
CO <sub>2</sub>	25.1	25.1%
C <sub>4</sub> H <sub>8</sub>	29.4	4.3%
C <sub>2</sub> H <sub>6</sub>	38.8	9.4%
C <sub>2</sub> H <sub>4</sub>	41.0	2.2%
O <sub>2</sub>	45.0	2.0%
CO	56.3	13.3%
H <sub>2</sub>	66.7	10.4%
Increase	36.8	29.9 cc.
C <sub>n</sub> H <sub>2n+2</sub>	58.0	21.3%
N <sub>2</sub>	12.0	12.0%
Average n	51.2 CO <sub>2</sub>	

$$\text{Average } n = \frac{51.2 (\text{CO}_2)}{21.3 (\text{C}_n\text{H}_{2n+2})} = 2.4$$

If a precise determination of saturated hydrocarbons is necessary, the gas is first analyzed in the normal way (i.e., as described above) and the exact average n value determined. This value must be corrected, as follows:

average n found	true average n
1	1.01
2	1.982
3	2.959
4	3.904

For example, 65% saturated hydrocarbons are found with a corrected average n of 2.755. A second sample is analyzed through CO and is then passed into the iodine pentoxide-sulfuric acid, before the hydrogen is burned. After 20 passes of 2 minutes each, it is found that 35 parts by volume has been absorbed by the solution with a constant factor of 0.15 (observed 5 times); i.e., 5 parts by volume (0.15 x 20) of ethane has been absorbed. The remainder is now burned over CuO and the H<sub>2</sub> and saturated hydrocarbons, consisting now only of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, determined. For example,

a true average  $n$  value of 1.833 is found by combustion of 30 parts by volume. Thus there are  $0.833 \times 30 = 25.0$  volume parts of ethane and 5.0 volume parts of methane. In total there are:

Saturated hydrocarbons: 65 ccs. of average  $n$  2.755  
Propane and butane: 32.0 ccs. (35 - 3)  
Ethane: 28.0 ccs. (25 + 3)  
Methane: 5.0 ccs.

65 ccs.  $C_nH_{2n+2}$  yielded 179.2 ccs.  $CO_2$   
- 28 ccs. ethane - 56.0 ccs.  $CO_2$   
- 5 ccs. methane - 5.0 ccs.  $CO_2$   

---

32 ccs. remainder 128.2 ccs.  $CO_2$

Average  $n$  of remainder =  $\frac{128.2}{32.0} = 3.69$

Butane = 22.1 ccs. (0.69  $\times$  32)  
Propane = 9.9 ccs.

Summary

65 ccs. of saturated hydrocarbons, average  $n$  2.755 of which

$C_4H_{10}$  = 22.1%  
 $C_3H_8$  = 9.9%  
 $C_2H_6$  = 28.0%  
 $CH_4$  = 5.0%

With old solutions the reaction proceeds considerably slower, and therefore they should be renewed frequently. The used iodine pentoxide solution is suitably treated to recover the iodine. In order to ready the apparatus for the next analysis, the combustion tube must be brought to a red glow and the reduced copper oxidized to  $CuO$  by oxygen or air. Oxygen as well as nitrogen for flushing the apparatus is drawn in through the 3-way stopcock of the compensator (1). This method, however, showed very poor agreement with Podbielniak analysis.

(1) Supplied by Ernst Haage, Mülheim/Ruhr, Neudecker Strasse 10.

Translated by D. M. Mason  
/lgn: March 27, 1946

a true average  $n$  value of 1.833 is found by combustion of 30 parts by volume. Thus there are  $0.833 \times 30 = 25.0$  volume parts of ethane and 5.0 volume parts of methane. In total there are:

Saturated hydrocarbons: 65 ccs. of average  $n$  2.755  
Propane and butane: 32.0 ccs. (35 - 3)  
Ethane: 28.0 ccs. (25 + 3)  
Methane: 5.0 ccs.

65 ccs.  $C_nH_{2n+2}$  yielded 179.2 ccs.  $CO_2$   
- 28 ccs. ethane - 56.0 ccs.  $CO_2$   
- 5 ccs. methane - 5.0 ccs.  $CO_2$   

---

32 ccs. remainder 128.2 ccs.  $CO_2$

Average  $n$  of remainder =  $\frac{128.2}{32.0} = 3.69$

Butane = 22.1 ccs. ( $0.69 \times 32$ )  
Propane = 9.9 ccs.

#### Summary

65 ccs. of saturated hydrocarbons, average  $n$  2.755 of which

$C_4H_{10}$  = 22.1%  
 $C_3H_8$  = 9.9%  
 $C_2H_6$  = 28.0%  
 $CH_4$  = 5.0%

With old solutions the reaction proceeds considerably slower, and therefore they should be renewed frequently. The used iodine pentoxide solution is suitably treated to recover the iodine. In order to ready the apparatus for the next analysis, the combustion tube must be brought to a red glow and the reduced copper oxidized to  $CuO$  by oxygen or air. Oxygen as well as nitrogen for flushing the apparatus is drawn in through the 3-way stopcock of the compensator (1). This method, however, showed very poor agreement with Podbielniak analysis.

(1) Supplied by Ernst Haage, Mülheim/Ruhr, Neudecker Strasse 10.

Translated by D. M. Mason  
/igm: March 27, 1946

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T46-98

API-TOM Reel 7<sup>a</sup> Frames 43-67  
Hydrierwerke-Pölitz A.-G.  
Main Laboratory  
Pölitz, April 10, 1942  
Investigations of Asphalts

Introduction

Coking chamber blow-down or other oils may contain foreign substances in true or colloidal solutions. In the following detailed statements the problem is treated which of these constituents it may be that influences the yield of oil on coking. The amount of benzol insoluble is decisive for the oil yield on coking, however, in addition to this there are still other materials present in the desolidified (Translator: solid-free?) oil, which act to diminish the oil yield. The structural build and the chemical multiplicity of these materials is unknown to us. Therefore our efforts can only aim to comprehend the totality of these substances, and to get their relation to the oil yield. The totality of these materials, which is contained in the product desolidified with benzol, we call the total-asphalt, without however declaring in this nomenclature, anything regarding the chemical properties of these materials. A certain fraction of this total asphalt, which however is characterized only by its analytical determination, we designate as part-asphalt.

The Determination of Total Asphalt

A 100 cc ground top Erlenmeyer flask is dried 1/2 hour at 150°C. and weighed without stopper after about 1/2 hour's standing over CaCl<sub>2</sub>. At the same time a porcelain filter crucible A<sub>1</sub> or a glass filter crucible G<sub>4</sub> is dried 1/2 hour at 150°C. and weighed after 1/2 hour's standing over CaCl<sub>2</sub>.

0.5 to 0.6 g. of the product to be investigated for asphalt is weighed into the Erlenmeyer flask, covered with 30 cc of benzol, and shaken for such length of time until no more oil adheres to the glass (about 5 min.).

The benzol solution is now separated from the benzol-insoluble by filtration, in which one filters through the porcelain or glass filter crucible. It is after-washed with about 300 cc of benzol. For more rapid washing out, one expediently stirs with a thin wire.

Erlenmeyer flasks and crucibles are dried 1/2 hour at 150°C. and weighed back after 1/2 hour's standing over CaCl<sub>2</sub>. The increase in the empty weight is added, and gives the benzol insoluble in the sample weighed in.

$$\% \text{ benzol insoluble} = \frac{\text{out-weight}}{\text{in-weight}} \times 100$$

A G<sub>4</sub> glass filter crucible is filled with 10 to 10.5 g. aluminum oxide (after Brockmann). The aluminum oxide consists of the part of the Brockmann preparation which has not passed a 100 DIN sieve. The G<sub>4</sub> crucible holds 30 cc.

The crucible with  $Al_2O_3$  is prepared as follows: after the weighing in of 10-16.5 g. of  $Al_2O_3$  in the crucible, the oxide is washed by suction three times with 10 cc benzol each time, then sucked dry, and dried at  $150^\circ C$ . for 1-1/2 hours. The crucible subsequently is allowed to stand exactly 1/2 hours over phosphorus pentoxide. (A glassy surface of the  $P_2O_5$  is to be destroyed each time.) Then the crucible is weighed. It is to be used as soon as possible after the weighing.

The benzolic filtrate (330 cc) is concentrated by distillation to 10 to 20 cc. The solution is then put on the  $Al_2O_3$  in the already prepared (as above described) crucible. The flask is after-rinsed with small portions of benzol, until it is washed out - in all about 10 cc. The suction speed should be regulated at a moderate rate, so that there is always a liquid layer over the  $Al_2O_3$  during the whole time of filtration. The washing medium amounts to exactly 200 cc of benzene. The benzene is poured on in such a way as not to disturb the aluminum oxide noticeably. After the washing-out, the material is sucked dry, allowed to dry 1-1/2 hr. at  $150^\circ C$ ., and weighed after standing exactly 1/2 hr. over  $P_2O_5$ . The difference in weight before and after adsorption corresponds to the "total asphalt" content of the weighed sample.

Calculation:

$$\% \text{ Total Asphalt in the sample} = \frac{\text{Final Weight (lit., out-weight) of Total Asphalt}}{\text{Initial Weight (lit., in-weight)}} \times 100$$

$$\% \text{ Total Asphalt in Oil} = \frac{10,000 \times \text{Final Wt. of Total Asphalt}}{(100 - \% \text{ Benzene-insoluble}) \times \text{Initial Wt.}}$$

$$= \frac{\% \text{ Total Asphalt in Sample}}{100 - \% \text{ Benzene-insoluble}} \times 100$$

The Determination of "Part-Asphalt"

In the determination of part-asphalt one proceeds exactly as in the determination of total asphalt. An alteration comes only when the benzene solution, concentrated to 10-20cc, is poured into the  $Al_2O_3$ -filled crucible. When, after washing out of the flask with ca. 100cc benzene, the sample is poured on the  $Al_2O_3$ , this is washed out with precisely 200cc ether, the suction is again regulated at a moderate rate, such that during the operation of washing out there always remains a layer of liquid standing over the  $Al_2O_3$ . Upon adding the ether the  $Al_2O_3$  must not be noticeably disturbed. Then the material is sucked dry and dried 1-1/2 hr. at  $150^\circ C$ . After leaving to cool for 1/2 hr. over  $P_2O_5$ , it is weighed. The per cent content of "Part-Asphalt" is calculated in an analogous way to that given for Total Asphalt.

Rapid Method for Determination of Total and Part Asphalt

The above-described methods for Total and Part Asphalt may be converted to rapid methods by proceeding as follows:

Definite fractions of the volume or weight of the  $Al_2O_3$  covered with Total- or Part-Asphalt are so mixed with various amounts by volume or weight of unused  $Al_2O_3$ , that the total volume or weight is equal to the original amount. In this way, by mixing, one prepares a color scale, with which the samples to be analyzed are compared. The total- or part-asphalt content of the comparison sample is thus known.

For the preparation of the samples for analysis one takes the same volume or weight of  $Al_2O_3$  as in the preparation of the comparison sample. One fills this  $Al_2O_3$  without drying into the G<sub>2</sub> crucible and pours the benzene solution, concentrated to about 10-20cc, upon the oxide, rinses out the flask with about 10 cc benzene as described, and re-washes with 200 cc benzene or ether. Then the crucible is placed in the drying cabinet until the odor of benzene has disappeared. Now, by streaking out, one compares the oxide in color with the comparison sample, and thus determines the content of total and part asphalt.

The comparison-preparations must be made from a product similar to that to be examined; otherwise substances of another shade might be present.

Examples on the Scattering of Analytical Values of the Total and Part-Asphalt Determination

Table 1 reproduces the values found for Total Asphalt by various analysts.

TABLE 1

<u>Blow-down from</u>	<u>Analyst</u>	<u>% Total Asphalt in Blow-down</u>	<u>% Total Asphalt in Oil</u>
Gelsenberg	I	20.75	27.78
	I	20.28	27.15
	II	20.64	27.65
	II	20.40	27.31
	III	20.58	27.55
	III	20.78	27.82
Pflitz	I	21.66	32.09
	I	21.68	32.12
	II	21.20	31.41
	II	21.39	31.69

In Table 2 the values found for Part Asphalt are reproduced.

TABLE 2

<u>Blow-down</u>	<u>Analyst</u>	<u>% Part-Asphalt in Blow-down</u>	<u>% Part-Asphalt in Oil</u>	<u>% Asphalt in Oil by Benzine (i.e. Petro- leum Ether Precipitation)</u>
Gelsenberg	III	9.66	12.92	11.7
	III	9.82	13.12	
	I	9.80	13.11	
Politz	I	9.40	13.9	14.0
	I	9.30	13.8	
	III	9.20	13.6	
Scholven	I	11.08	15.2	15.4
		11.40	15.5	

In the last division of Table 2 are given the asphalt values found by the method of precipitation with "normal benzene" (Tr. precipitation asphalt). If we compare them with the Part Asphalt values, we see that the asphalt values by the two methods agree. Through this the new methods of asphalt determination are connected with the methods used up to the present.

If we observe also the scattering of analytical values, we can say that the new methods lead to satisfactory results.

The Relations of the Total and Part Asphalts to the Yields in Operation

The total-asphalts are significantly higher than the part-asphalts. This enables us to distinguish easily which asphalt is a measure of the yields on coking of residue (Tr. the same word "Abschlamm", has been translated in differently as residue or blowdown). To get a judgement upon this relation, we set up the trivial relations 1 and 2.

$$\begin{aligned} \text{(N.A.)} &= P-A && - - 1 \\ \text{(N.A.) } F_1 &= K-(G.A.)F_2-DB-P.F_3 && - - 2 \end{aligned}$$

Here (the symbols) mean:

- (N.A.) - undecomposable
- K - coke
- (G.A.) - "Total Asphalt"
- DB-P - difference between benzene - and pyridine - insoluble
- F<sub>1</sub> - coking factor for the (N.A.)
- F<sub>2</sub> - " " " " (G.A.)
- F<sub>3</sub> - " " " " DB-P
- P - pyridine insoluble
- A - ash



The coking factors give the number by which the weight of charge must be multiplied to obtain the coke. The factors can be determined empirically. The following values were found:

$$F_1 = 0.92$$

$$F_2 = F_3 = 0.43$$

Coking was done with the Bochum crucible for 5 minutes in the electric furnace at 800°C. Table 3 gives an insight into the scatter of the analytical values.

TABLE 3

<u>Residue</u> <u>(i.e. Blowdown)</u>	<u>Coking Residue</u>	<u>Coke</u>
Gelsenberg	32.28	17.24
	32.20	17.16
Politz	39.70	15.30
	39.42	15.02
Scholven	38.88	31.85
	39.02	31.99

The definition of coke is:

$$\text{Coke} = \text{Coking Residue} - \text{Ash}$$

Equation 1 gives directly a definition of non-decomposable (N.A.) and indeed is equal to the pyridine-insoluble less the ash.

That the non-decomposable (N.A.) is not exclusively elementary carbon, follows from the fact that other solvents, especially solvent mixtures, can extract still a further portion. Table 4 reproduces a few data with reference to this.

TABLE 4

<u>Residue</u>	<u>Solvent</u>	<u>Insoluble</u>
Politz	Pyridine	25.74
		26.15
	Benzene-Pyridine (1:1)	25.11
		24.73
	CS <sub>2</sub> -Benzene (1:1)	27.62
		28.08
	CS <sub>2</sub> -Pyridine	24.99
		25.32

The fact that the coking factor is less than 1 also signifies that the non-decomposable is not exclusively elementary carbon.

Equations 1 and 2 are independent of each other. The Total Asphalt value enters into Equation 2 and not in Equation 1. The calculation of non-decomposable (N.A.) or the factor  $F_1$  must lead to the same values, for both equations, if the Total Asphalt is a measure of the coking.

The necessary data for this calculation can be drawn from Table 7.

Calculation for Pöhlitz Residue (The Values are Referred to 100g. Residue)

$$\begin{aligned}(\text{N.A.}) &= P-A \\ 13.1 &= 27.5-14.4 \\ (\text{N.A.}) F_1 &= K-(G.A.) F_2 - D_B - P F_3 \\ 13.1 F_1 &= 25.1-21.5 \times 0.43 - 5.0 \times 0.43 \\ 13.1 F_1 &= 13.7 \\ F_1 &= 1.0 \quad (\text{Experimental } F_1 = 0.92)\end{aligned}$$

The agreement between the calculated and found values can be called good.

Calculation for Gelsenberg Residue (Values Referred to 100g. Residue)

$$\begin{aligned}(\text{N.A.}) &= P-A \\ 8.0 &= 23.0-15.0 \\ (\text{N.A.}) F_1 &= K-(G.A.) F_2 - D_B - P F_3 \\ 8.0 F_1 &= 17.2-20.5 \times 0.43 - 2.3 \times 0.43 \\ 8.0 F_1 &= 7.4 \\ F_1 &= 0.92 \quad (\text{Experimental } F_1 = 0.97)\end{aligned}$$

The agreement between  $F_1$  calculated and  $F_1$  experimental is again good.

If, however, we substitute the values for the Part Asphalt in Equation 2, then the calculated coking factors become:

$$F_1 \text{ (Pöhlitz Part Asphalt)} = 1.5$$

$$F_1 \text{ (Gelsenberg Part Asphalt)} = 1.5$$

There is no agreement with the experimental values of  $F_1$  ( $F_1 = 0.92$ ). Therefore, it appears that only the Total Asphalt gives a measure of the yields in residue coking. Since the Part Asphalt agrees with the asphalt values obtained by the naphtha precipitation method, it appears that the previously used asphalt values do not give a measure for estimating the coking yields.

Calculation for Scholven Residue (The Values are Referred to 100g. Residue)

$$\begin{aligned}
 (N.A.) &= P-A \\
 10.1 &= 17.1-7.0 \\
 (N.A.) \times F_1 &= 31.92-25.3 \times 0.43-9.2 \times 0.43 \\
 10.1 \times F_1 &= 14.9 \\
 F_1 &= 1.5
 \end{aligned}$$

This value for  $F_1 = 1.5$  does not agree with the experimentally found value (0.92). If for Scholven residue we substitute the value for Part Asphalt in Equation 2, we obtain:  $F_1(\text{Scholven, Part Asphalt}) = 2.3$ .

Both factors are too high in comparison with the experimentally determined value ( $F_1=0.92$ ). This indicates that Equation 2 can be used upon Scholven residue only in a further developed form. Specifically, the following must hold:

$$(N.A.) \times F_1 = K-(G.A.) \times F_2-D_{B-P} \times F_3-(Oil) \times F_4 \dots\dots 3$$

Or, in other words, the asphalt-free oil in Scholven residue possesses a coking residue. The coking factor of the oil is  $F_4$  and was found to be  $F_4 = 0.18$

If we substitute this value of  $F_4$  and the Total Asphalt in Equation 3, we obtain:

$$\begin{aligned}
 (N.A.) \times F_1 &= 8.4 \\
 10.1 \times F_1 &= 8.4 \\
 F_1 &= 0.84 \quad (\text{Experimental } F_1 = 0.92)
 \end{aligned}$$

This agreement between  $F_1$  calculated and  $F_1$  experimental can also be called good.

In summary it may be said that the Total Asphalt alone is important in residue coking.

In Table 5 we assemble the results of these calculations.

TABLE 5

<u>Residue</u>	<u><math>F_1</math> (calculated) for Total Asphalt</u>	<u><math>F_1</math> (calculated) for Part Asphalt</u>	<u><math>F_1</math> (experimental)</u>
Pöhlitz	1.0	1.5	0.92
Gelsenberg	0.92	1.5	0.92
Scholven	0.84	1.5	0.92

Based on 100g Residue

Source	Ether-insoluble	Benzene-insoluble	Pyridine-insoluble	D <sub>B-P</sub>	D <sub>A-B</sub>	D <sub>A-P</sub>	Ash	Coking Residue
Poltz Ka 13	37.7	32.5	27.5	5.0	5.2	10.2	14.40	39.51
Gelsenberg	27.0	25.3	23.9	2.3	1.7	4.0	15.04	32.24
Schölvén	35.5	26.3	17.1	9.2	9.2	18.4	7.03	38.95

Meaning (of symbols)

D<sub>B-P</sub> : Benzene - minus pyridine-insoluble

D<sub>A-B</sub> : Ether - " benzene "

D<sub>A-P</sub> : Ether - " pyridine "

Coke means coking residue minus ash

Calculating factors for residue to oil:

$$F^{\text{P}}(\text{Poltz}) = 1.48$$

$$F^{\text{G}}(\text{Gelsenberg}) = 1.34$$

$$F^{\text{S}}(\text{Schölvén}) = 1.36$$

Source	Based on 100% residue										Based on 100 E Oil (Oil is given by residue less benzene-insoluble).										% asphalt in naphtha precipitation of oil.			
	Poite No. 13	Polite No. 13	Scholven	Polite No. 13	Polite No. 13	Scholven	Polite No. 13	Polite No. 13	Scholven	Polite No. 13	Polite No. 13	Scholven	Polite No. 13	Polite No. 13	Scholven	Polite No. 13	Polite No. 13	Scholven						
Ether-insoluble	37.7	32.5	27.5	5.0	5.2	10.2	14.40	39.51	25.11	21.5	9.8	55.8	48.1	40.7	7.4	7.7	15.1	21.31	58.48	37.17	31.8	19.5	14.0	
Benzene-insoluble	27.0	25.3	23.9	2.3	1.7	4.0	15.04	32.24	17.20	20.5	9.5	36.2	33.9	30.8	3.1	2.3	5.4	20.15	43.30	23.05	27.5	12.7	11.7	
Pyridine-insoluble																								
D <sub>B-P</sub>																								
D <sub>A-B</sub>																								
D <sub>A-P</sub>																								
Ash																								
Coking Residue																								
Coke																								
Total Asphalt																								
Part Asphalt																								
Ether-insoluble																								
Benzene-insoluble																								
Pyridine-insoluble																								
D <sub>B-P</sub>																								
D <sub>A-B</sub>																								
D <sub>A-P</sub>																								
Ash																								
Coking Residue																								
Coke																								
Total Asphalt																								
Part Asphalt																								

D<sub>B-P</sub> : Benzene - minus pyridine-insoluble  
 D<sub>A-B</sub> : Ether " " benzene "  
 D<sub>A-P</sub> : Ether " " pyridine "  
 Coke means coking residue minus ash  
 Calculating factors for residue to oil:  
<sup>1</sup>(Poite) = 1.48  
<sup>2</sup>(Galsenberg) = 1.34  
<sup>3</sup>(Scholven) = 1.36

TABLE 7

In Table 6 the ratio of Part Asphalt to Total Asphalt is shown.

TABLE 6

<u>Residue</u>	<u>Part-/Total-Asphalt</u>
Flitz	0.46
Gelsenberg	0.46
Scholven	0.45

The ratio of Part- to Total-Asphalt

$$\frac{\text{Part-Asphalt}}{\text{Total-Asphalt}} = A \dots\dots 4$$

is of the same magnitude in the samples examined. This, however, must not always be so. On the contrary, the value of A gives a deep insight into the composition of the oil.

In Table 7 is a collection of all determined values. We see from this table that not only the asphalt values, but all values entering into Equations 2 and 3 are of significance. Table 7 also shows that with high asphalt content,  $D_{p-p}$ , coke, etc. are also high. All further relationships can be seen from the table itself, so nothing further will be needed here on that subject.

General Observations

For the exact working out of the analytical method, it was necessary to test, in the removal of solids (Entfesten), to what extent the amount dissolved depended upon time. Table 8 shows that the process of solution is completely over in less than 1/2 hr.

TABLE 8

<u>Solvent</u>	<u>Duration of Solution Process, in Hours</u>	<u>Insoluble %</u>
Benzene	1/2	28.28
"	1/2	28.02
"	4	27.75
"	4	28.15
"	4	28.05
"	shaken 4	28.02

In Table 9 the data are given on the influence of the amount of solvent on the solution process. With ether and benzene 30 cc. of solvent are sufficient to desolidify about 0.5 g.

TABLE 9

<u>Solvent</u>	<u>cc Benzene</u>	<u>cc Ether</u>	<u>cc Naphtha</u>	<u>Solid (Insoluble)</u>
Benzene	30	-	-	32.41; 32.76
	60	-	-	32.40; 32.76
	90	-	-	32.66
Ether	-	30	-	37.56; 37.85
	-	60	-	38.09; 37.78
Naphtha	-	-	30	57.28; 54.46
	-	-	60	48.94; 50.01

As is known, the solvent influences the amount of insoluble solids. Table 10 shows the amount of insoluble solids for several solvents.

TABLE 10

<u>Solvent</u>	<u>% (insoluble) solids, Politz</u>	<u>% (insoluble) solids, Gelsenberg</u>	<u>% (insoluble) solids, Scholven</u>
Benzene/Pyridine (1:1)	24.62		
CS <sub>2</sub> /Pyridine (1:1)	25.25		
Pyridine	25.93	22.88	17.15
CS <sub>2</sub>	26.01	24.70	24.88
CS <sub>2</sub> /Benzene (1:1)	27.85		
Benzene	27.98	25.33	26.35
Ether	35.00	26.79	35.91
Naphtha	48.28	39.35	

Summary

New analytical methods were worked out for determining Total- and Part-Asphalt.

The Part-Asphalts are identical with the asphalt values obtained by naphtha precipitation (Footnote 1).

The Total-Asphalts alone enter into Equations 1 to 3 and determine the oil yields upon coking.

FOOTNOTE 1: With products which were investigated after this work, this observation was not always confirmed.

We are now in a position to give the theoretical coking yields. They are calculated from Equation 5.

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} \times f_1 + \text{Total Asphalt} \times f_2 + \text{Gas}) \dots \dots \dots 5$$

For the case where the oil itself has a coking residue, Equation 6 holds:

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} \times f_1 + \text{Total Asphalt} \times f_2 + \text{Gas} + \text{Oil} \times f_0) \dots \dots \dots 6$$

As an approximate equation, there holds:

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} + \text{Total Asphalt}) \dots \dots 7$$

This approximate equation always holds when the volatile components upon coking of the benzene-insoluble end of the Total Asphalt give gas exclusively. A second approximate equation holds when the oil itself has a coking residue.

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} + \text{Total Asphalt} + \text{Oil} \times f_0) \dots \dots \dots 8$$

All values in Equations 5-8 are referred to 100g. residue. If one calculates the oil yield as usual upon 100g. oil, then this value is obtained from Equations 5-7 by the following additional calculation:

$$\frac{g. \text{ Oil from 100g. Residue}}{100 - \text{Benzene-insoluble}} \times 100 = \text{Oil Yield/100g. Oil} \dots \dots \dots 9$$

If we carry through the calculation for Politz residue by approximate Equation 7 and convert to (the basis of) oil by Equation 9, we get:

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} + \text{Total Asphalt}) \\ = 100 - (32.5 + 21.5) \\ = 46$$

$$g. \text{ Oil Yield/100g. Oil} = \frac{g. \text{ Oil from 100g. Residue}}{100 - \text{Benzene-insoluble}} \times 100 \\ = \frac{46}{67.5} \times 100 \\ = 68.1$$

This yield is too low, thus the approximate equation is therefore not usable.

We carry through the calculation with Equation 5:

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} \times f_1 + \text{Total Asphalt} \times f_2 + \text{Gas}) \\ = 100 - (32.5 \times 0.94 + 21.5 \times 0.43 + 5) \\ = 55.2$$



$$\begin{aligned} \text{g. Oil Yield/100g. Oil} &= \frac{\text{g. Oil from 100g. Residue}}{100 - \text{Benzene-insoluble}} \times 100 \\ &= \frac{55.2}{67.5} \times 100 \\ &= 82 \end{aligned}$$

82% would be, according to the present investigations, the maximum oil yield attainable. This result naturally agrees with practice only so long as no catalyst or other materials are present, to which might come the ability to convert asphalts into liquid products.

The approximate equations are not usable in our case. It is seen directly from the factors for asphalt coking, that with high asphalt content the approximate equations cannot hold, since the loss to gas does not rise correspondingly with the asphalt content.

In Equations 5 to 10 (the symbols) mean:

$$\begin{aligned} f_0 &= \text{Coking factor of the oil} = 0 \\ f_1 &= \text{" " " " benzene-insoluble} = 0.94 \\ f_2 &= \text{" " " " Total Asphalt} = 0.43 \end{aligned}$$

$f_0$  is zero for Politz and Gelsenberg residue, and 0.18 for Scholven residue

In conclusion it should be emphasized that the time required for analysis in asphalt determination by naphtha precipitation amounts to about 20 hrs.; by the present method an asphalt determination takes only 5 hours.

(Trans.: this statement is questioned marginally on German original.)

/s/ Wickert

Frame 57 shows a drawing of apparatus for asphalt determination.

APPENDIX to the Report

"Investigations of Asphalts"

In the following expressions it is attempted to use the results of the report "Investigations of Asphalts" upon our coking operation.

The oil yield based on 100g. residue, is calculated as follows:

$$g. \text{ Oil from 100g. Residue} = 100 - (\text{Benzene-insoluble} \times 0.94 + (\text{Total Asphalt}) \dots 1$$

If the ash content in the residue varies strongly, then Equation 1 is to be written as follows:

$$g. \text{ Oil from 100g. Residue} = 100 - ((\text{Benzene-insoluble} - \text{Ash}) \times f_1 + \text{Ash} + \text{Total Asphalt} \times 0.43) \dots 2$$

The yield of oil per 100g. oil is given by Equation 3:

$$g. \text{ Oil/100g. Oil} = \frac{g. \text{ Oil from 100g. Residue}}{100 - \text{Benzene-insoluble}} \times 100 \dots 3$$

In Equations 1-3 (the symbols) mean:

- Benzene-insoluble - Benzene-insoluble in 100g. residue
- (G.A.) = Total Asphalt - Total Asphalt in 100g. residue
- 0.94 - Coking factor for the benzene-insoluble
- 0.43 - " " " " Total Asphalt
- f<sub>1</sub> - " " " " (Benzene-insoluble - ash)

In Table 1 are given the calculated oil yields, and the analytical results (1), which were used. Also in Table 1 we find the oil yields from operation.

The calculated oil yields on the various days are again given in curve I. Curve II shows the corresponding oil yields in operation.

We see from the curves, that the calculated oil yields lie higher than those from operation. The difference of ordinates between I and II affords an insight into the manner of operation of the process. The difference I-II varies between 0.6-0.8 in the first part of the curves. Only on April 24 does it lie higher - actually at 1.8. On this day there was,

(1) The analyses are done in the Oil and Coal section of the Main Laboratory.

however, according to indications, a disturbance in operations, which explains the high value of 1.5. On April 30 the difference reaches 1.0 which only begins to fall on May 10. For this behavior also there was an explanation from the operation itself; the cause lies in the after-effects of a disturbance of operation which occurred before May 4.

TABLE 1

<u>Date</u>	<u>Total-Asphalt in 100g. Residue</u>	<u>Benzene insol.</u>	<u>Ash</u>	<u>Oil Yield (calculated)</u>	<u>Oil Yield (operational)</u>
13 Apr. 42	23.1	23.0	9.7	89.1	81
14 " "	23.1	23.2	10.3	88.8	80
15 " "	23.3	23.5	10.8	88.8	79
19 " "	26.5	22.0	9.0	88.9	80
23 " "	23.2	21.5	8.8	89.0	83
24 " "	25.6	21.5	8.8	87.8	76
26 " "	27.0	23.0	9.2	88.7	80
27 " "	27.0	23.0	9.4	88.7	81
28 " "	28.8	24.6	10.4	85.5	81
29 " "	24.2	22.0	9.2	88.6	85
4 May "	26.2	23.0	9.6	86.0	77
5 " "	27.3	23.8	10.8	86.4	75
7 " "	25.6	23.7	10.6	87.5	78
10 " "	22.7	23.4	11.0	89.1	80
11 " "	27.4	23.4	10.8	86.4	81
12 " "	23.4	23.3	10.2	88.6	82
13 " "	26.2	23.8	10.5	87.0	78

Under normal operating conditions the operating oil-yield falls or rises when the calculated oil yield falls or rises. This shows again that the benzene-insoluble and the Total Asphalt are a measure of the coking yield.

If one does not work with diagrams, it is useful to give the yields by factors.

For Example:

$$\text{Oil yield (calc.)} \times F = \text{Oil yield (from operation)}$$

The average value of a factor over a month gives a good insight into the yield attained.

The average factor from the dates given here is about 0.96.

/s/ Wiekert

### 3. COMMUNICATION

#### Summary Report on the Investigations Completed to Date in Scholven, for the Development of a Special Method for Asphalt Decomposition

##### Connection of research results with various operating data.

As has been communicated earlier (cf. 1st and 2nd file memorandum on asphalt decomposition December 5, 1940 and January 13, 1942), it is always confirmed again from operations that the asphalt values obtained by the S- asphalt determination cannot be brought into any proper correspondence with operating data. Thus for example, extraction residues have behaved altogether differently in coking, although they showed the same content of benzene-insoluble and the same S- asphalt content in the oil. We must therefore consider that in the S- asphalt determination in the benzene-soluble part of the product examined, either not all of the asphalt important for coking was collected, or else the asphalt composition in these residues is different.

Therefore researches were undertaken, to replace the present separation of hydrogenation products into ash, benzene-insoluble, S- asphalt and asphalt-free oil by another method of examination, which will permit the benzene-insoluble and asphalt fractions of the hydrogenation product to be further broken up, in order to understand the connection with operating data on the chambers, and with coking properties. Special value was laid on finding a method as simple as possible, with which good reproducible values could be obtained quickly, without a great supply of apparatus.

##### Results of the I.G. Lu (Ludwigshaven?) Proposed Method for Asphalt Analysis

The first investigations carried out, according to a procedure of the I.G. Lu (Ludwigshaven), in which the pyridine- $CS_2$  soluble part of the hydrogenation product was separated with the aid of solvent, precipitation and adsorption media into neutral oil, oil resin, resin formers, asphalt resins, asphaltenes, carbones and carboids, resulted, mainly perhaps on account of the lack of exact data on the amounts of the solvents and adsorbents to be added, in such highly scattered values, that no further conclusions could be drawn from them.

##### The Method of Suida and Motz as Altered in Scholven

These sources of error were avoided in the method developed by Suida and Motz (Petroleumzeitchrift 35 (1939) 527) for the analysis of natural asphalts, so that with it there was no such scattering of values. For the examination of hydrogenation products this method was altered and broadened by us in several points. In contrast to the above-mentioned I.G.-method the product to be examined was used as such, with its whole ash and solid content, and not the pyridine- $CS_2$  soluble part of the product alone, since in our experience it is rather difficult to remove pyridine completely from the solids-free extract without at the same time driving off light oils and altering the dissolved asphalt and resin components. Since, however, in the

Suida extraction one extracts first with a poorer solvent than pyridine, the complete removal of pyridine is necessary. Therefore, we dissolve the product to be examined (about 1.5g.) in 30cc chloroform, and put this solution, with the solids contained in it, into the apparatus described by Suida and Motz, for extraction with chloroform at 20° and next with pyridine at 20° and 60°. To this extraction proposed by Suida and Motz we add a 2 hour extraction with pyridine-CS<sub>2</sub> 1:1 mixture at 38°, to extract the less readily soluble asphalts also.

In the chloroform extract, after complete removal of chloroform at not more than 100°, we also determined the resins which precipitate with normal naphtha. For this the residue from the CHCl<sub>3</sub>-extract (neutral oil and oil resins) was dissolved in 5cc benzene, and the resins were precipitated with 100cc of Kahlbaum normal naphtha (Normalbensin), and determined further as with 8- asphalt. Precipitation with normal naphtha without addition of benzene is not recommended, for then the oil resins precipitate out in lumps, carrying neutral oil with them, which can hardly be all dissolved out of the oil resins even by rinsing with normal naphtha.

The working up of the pyridine extract was originally carried out by us also according to Suida and Motz, but more recently we have proceeded otherwise, for it was ascertained that the asphalts in pyridine solution, after the pyridine is dissolved out with dil. HCl, will dissolve only partially in CS<sub>2</sub>, because CS<sub>2</sub> alone is a poorer solvent for asphalts than is pyridine. Therefore we filter the pyridine- and pyridine-CS<sub>2</sub> solutions, (after distilling off most of the solvent) through a thick paper filter and dissolve the pyridine still present (110-120cc) by slow addition of dil. HCl. The flocculent precipitated asphalts thus obtained are filtered through a porcelain filter crucible, washed with distilled water, and weighed after drying in a drying cabinet at 100°.

In this manner one gets a separation of the hydrogenation product into the following components:

- (a) CHCl<sub>3</sub> - soluble at 20°
  - (a<sub>1</sub>) neutral oil
  - (a<sub>2</sub>) oil resins (precipitated with normal naphtha)
- (b) pyridine soluble at 20°  
asphalt resins
- (c) pyridine-soluble at 50°  
hard asphalt
- (d) pyridine-CS<sub>2</sub>-soluble at 38°  
asphaltenes, carbenes, carboids
- (e) pyridine-CS<sub>2</sub>-insoluble (calculated to make up the difference between 100 and the sum of the above values, because a direct weighing of the mixture with Terrana earth is impossible)

The modified Suida method gives good reproducible values (see Table 2). It is certainly important that they agree in their measurement when working with different apparatus. The value for pyridine- $CS_2$ -insoluble is inexact, because it is calculated as a difference between 100 and the sum of the values (a) to (d).

Upon observing the experimental data collected in Fig. 1b and 1c obtained by this procedure upon different residues and pressed oils, it is striking that the substances extracted by pyridine at  $50^\circ$  (Hard Asphalt) and by pyridine- $CS_2$ -mixture (asphaltenes) are small in amount in almost all samples, and nearly independent of the nature of the sample. After extraction of the neutral oils and oil resins with chloroform at  $20^\circ$ , the greater part of the remaining extractable material is dissolved out by pyridine at  $20^\circ$ , while only a little more is extracted by pyridine at  $50^\circ$  and by pyridine- $CS_2$ . The asphalt resin extracted with pyridine at  $20^\circ$  thus corresponds to almost the total asphalt contained in the product. One thus does not get any sufficient separation of the asphalts into several fractions. To accomplish this, one should, after the extraction with chloroform at  $20^\circ$ , use next a less sharply acting solvent than pyridine, in order to extract only a part of the pyridine-soluble asphalt. Next, after this, one should dissolve out more asphalts with pyridine at  $20^\circ$ .

In the Suida method as in the other methods described in the literature for analysis of asphalt, it is always attempted to isolate the extracted asphalt components, in order to examine them further. This procedure has the disadvantage that great amounts of solvents must be very carefully driven off, always running the danger that the resin and asphalt components will be chemically changed or that the solvent will induce such reactions, for example with the oxygen of the air. Thus recently Carlsohn and Eicke (Z. angew. chem. 54 (1941) 520) indicated that, for these reasons, O-, N- and S-containing solvents cannot be used for asphalt extraction.

We were able to confirm this in researches with pyridine. We added the purest pyridine, which left practically no residue upon distillation, to Topp residue, and then very carefully drove off the pyridine from the Topp residue-pyridine mixture, at  $180^\circ$ , until constant weight was obtained. In contrast to a sample dried to constant weight at  $180^\circ$  without added pyridine, the pyridine treated samples always showed a weight increase of 2.5 to 4% (based on the amount of Topp residue), even when the pyridine was driven off in the absence of air in a heated vacuum desiccator. It is thus also made plain that one finds much too high asphalt resin, hard asphalt and pyridine- $CS_2$  soluble values in the Suida method, if one drives off the last of the pyridine with heat and does not want to dissolve it out with dil. HCl.

Therefore, in the isolation of resin and asphalt components from extracts, one must always keep in mind that under (some) conditions they are chemically changed by the solvent and form resins with the solvent, so that excessively high weights may be found.

#### New Method Proposed by Scholven for Asphalt Analysis

Since we did not think it useful to complicate the Suida method by introducing further solvents, and also wished to avoid as thoroughly as possible the changes caused by the effect of the solvent on the dissolved material, a new method was developed in Scholven for analyzing hydrogenation products, in which we consciously abandoned (any attempt) to isolate the various resin and asphalt components as such. As in the solids determination with benzene, separate determinations were made of the fractions of the hydrogenation product insoluble in  $\text{CCl}_4$ , benzene, chloroform and pyridine, and these values were related to each other. To include also the  $\text{CCl}_4$ -soluble resin, we also carried through a separation of the  $\text{CCl}_4$ -solubles into neutral oil and oil resin, in the Suida apparatus using  $\text{CCl}_4$  as solvent and Ferraza earth as adsorbent, in which determination only the neutral oil is determined, the resin content is calculated from this and from the total  $\text{CCl}_4$  soluble.

This analytical method is simple and rapidly done, and requires only little apparatus, so that it may be used for the operating analysis of residues and other products, instead of the thus far used S- asphalt determination and the modified Suida method. Here the use of precipitants is altogether avoided, and the use of adsorbents avoided as far as possible. It was only in the determination of neutral oil in the  $\text{CCl}_4$ -soluble fraction that the use of Ferraza earth and the Suida method could not be escaped. If, instead of this solvent, one could use a solvent which dissolved out practically only neutral oil and no resins, then upon the addition of this solvent, e.g. petroleum, ether, the asphalts and resins of the residue would precipitate out in lumps so as to carry along much neutral oil and thus ruin the determination. Since the components insoluble in the solvent used are always determined outside of the neutral oil determination, the effect of the solvent on the dissolved material is excluded. In the neutral oil determination this effect would be of no significance, since this oil contains almost no resins, but neutral oil, which does not alter under the influence of solvent and atmospheric air.

The determinations are carried out as follows:

- (a) Determination of  $\text{CCl}_4$ -, benzene-, chloroform-, and pyridine-insoluble.

In each case 1-2g. of the product to be analyzed is boiled in a 100cc Erlenmeyer with 50cc of the solvent used, for 1/2 hr., under a reflux condenser<sup>(1)</sup>. It is then filtered through a porcelain filter crucible and rinsed clear with hot solvent. The residue is dried in a drying cabinet at 100° (the pyridine-insoluble at 120°) and weighed.

Footnote 1: According to later experiments, 1/4-hour boiling is sufficient.

(b) Determination of neutral oil in the  $\text{CCl}_4$ -soluble fraction.

1.5 g. of the product to be examined is boiled with 50cc  $\text{CCl}_4$  under reflux for 1/2 hr., as above. Then the contents of the Krlenmeyer flask, after cooling, are dripped into a suspension of 10g. Torrona earth in 200cc  $\text{CCl}_4$ , in the asphalt analysis apparatus of Suida and Metz, over a period of about 1/2 hr., and extracted for 3 hr. at  $20^\circ$ . For better constancy of temperature the extractor was surrounded with a water-jacket held at  $20^\circ$  by a thermostat. After the end of the extraction the extract is removed, the solvent distilled off, and the last cc of  $\text{CCl}_4$  driven off in the drying oven at  $80^\circ$ . The residue is weighed and reported as neutral oil.

The simply carried-out insoluble-determinations give very reproducible values. (See Table 2). Longer boiling of the complex under reflux, e.g. 2 hr., gives practically the same values. The neutral oil extracted in the Suida apparatus still contains in general 0.5-3% of resin fractions which will precipitate with normal asphalts. This error can be taken into account.

By forming from the determined values the differences of each pair of consecutive solubility values and in addition the difference between the  $\text{CCl}_4$  soluble and the neutral oil, one obtains an analysis of the hydrogenation products into components which we have indicated by the following names:

1. Ash in the product.
2. Ash-free pyridine-insoluble = pyridine-insoluble minus ash.
3. A - Asphalt (the most difficultly soluble asphalt)  
- = chloroform-insoluble minus pyridine-insoluble.
4. B - Asphalt = benzene insoluble minus chloroform-insoluble.
5. C - Asphalt (easily soluble asphalt) =  $\text{CCl}_4$ -insoluble minus benzene-insoluble.
6. Oil resin =  $\text{CCl}_4$ -soluble minus neutral oil.
7. Neutral oil.

A series of residual and pressed-oil examinations were done in this way (see Fig. 1a, 2a, Table 1 and 2). Their results will be discussed in the second section in connection with operating data.

FRAMES 68-73

II. (This section gives comparison with operating data. Not translated). One mention is made of a "contact" of 0.03%  $\text{SnO}_2$  + 0.12% Pb added to coal tar pitch for processing.

Translated by R.E. Florin, December, 1946  
Typed 2/17/47  
Information Division Translation T46-98



*Standard Oil Company (Indiana)*

INFORMATION DIVISION TRANSLATION T47-16

API-TOM Reel 14, Frames 798-801  
Palatinol from Oxo Alcohol

We have requested Leuna to separate Oxo alcohol, boiling in a relatively wide range, into four fractions, in order to establish (1) how the Palatinols prepared from the separate fractions behave in utilization technique, and (2) from which fraction is to be expected the Palatinol with the best properties.

In addition to this we are interested to learn whether the highest-boiling fraction still will produce a useful softener, since according to previous observations in the processing of these high-boiling portions, the unesterifiable constituents are removed only with difficulty from the Palatinols by steam- or vacuum-steam-distillation.

Finally, the investigation should serve to define obligatory sales restrictions for the Oxo alcohols.

We have esterified the fractions of alcohol transmitted to us from Ammoniakwerk Merseburg, Stickstoff-Abteilung, with a letter of May 9, 1944, along with the unfractionated alcohol (charge product). This was done with phthalic anhydride, with use of sulfuric acid (0.5% \* calculated on phthalic anhydride) as the catalyst, which was buffered with alpha salt (1.3% calculated on phthalic anhydride), and toluol as the water carrier; at times an excess of 10% alcohol was used (calculated on hydroxyl content).

The attached tables inform you regarding our operating results.

\* This figure is not clear - might be 0.35 or 0.95%.

Summary

A high percentage of alcohol exists in the transmitted Oxo alcohol, which actually permits better processing than earlier deliveries.

Conditional upon the results of technical utilization testing, it seems to us, on the basis of previous investigations and in regard to technical operating considerations (esterization velocity, removal of unesterified portions from the Palatinol, yield), expedient in the future to leave out of the deliveries not only the alcohol fraction 94-160°C. (fractionally 5%) but also the fraction 220-240°C. (fractionally 7.8%), and to cut off correspondingly closer.

In our opinion, such a limitation of the boiling range permits expectation of a uniform finished product, since (1) only alcohols of the C8 and C9 series are processed, and (2) because the non-esterifiable constituents contained in these alcohols still permit removal sufficiently easily by means standing available to us in operations.

Offenbach-Orlean  
June 29, 1944.

Offenbach Works  
Operations Division

Palatinol from OXO Alcohol

	OXO ALCOHOL				RESULTS ON THE ESTERIFICATION										YIELD				
	% Reaction	Boling Interval	Sp. Grav.	% OH	OH Number	Mol. Weight	Sp. Grav.	Flash Point	Neutralization Number	Saponification Number	Viscosity	Aster M.V.	Alcohol M.V.	Average Chain Length Alcohol	Ketorizable Portion of Alcohol	% of Charge Phthalic Acid	% of Theoretical	% of Charged Alcohol	% of Alcohol
Oxo Alcohol not fractionated (Charge)	100	160-240° C	0.830	10.75	354	156.1	0.9964	215° C	0.056	272.6	116.2op.	410.8	140.4		88.9%	223.0	80.3	94.2 (86.9)	100.7
Fraction I	5.0	94-160° C	0.797	4.35	143	390.8	1.0255	-	.224	352.7	49.0	317.6	93.8	5.41	24.6%	148.6	69.6	18.6 (24.0)	77.4
Fraction II	48.3	160-200° C	0.851	12.17	401	139.7	0.9969	200°	0.056	286.5	89.0	390.9	190.4	8.03	93.4%	237.8	90.1	114.6 (93.4)	122.8
Fraction III	35.6	200-220° C	0.860	11.11	366	153.0	0.9945	208°	0.028	265.5	163.5	421.8	145.4	9.1	93.0%	250.0	57.7	110.1 (95.0)	115.9
Fraction IV	78	220-240° C	0.866	9.32	307	182.4	0.9895	-	0.084	246.9	201.7	453.6	161.8	10.3	86.7%	244.6	79.8	90.28 (88.7)	101.8
Mixture of Fractions II and III in ratio 46.3 : 36.6	83.9						0.9566	-	0.1	275.3	117.2	406.8	138.4	8.6		244.6	89.0	113.1 (effortive)	

\* The OH numbers and the apparent molecular weight are calculated from % OH.

\*\* Calculated from the saponification number of the Palatinol.

For testing the correctness of our view, we have prepared a Palatinol from a mixture of Fractions II and III (mixture ratio 48.3:35.6, that is corresponding to the percentage portion); the results likewise are contained in the table.

It was of interest to establish, in connection with this work, how high the portion of secondary alcohols is in the charge material.

According to our observations, in a mixture of primary and secondary alcohols, under suitable conditions, only the primary alcohols convert to the phthalic acid mono-ester.

We have now treated the unfractionated Oxo alcohol in this manner, and non-esterifiable portions separate in amount of 11.2% (density = 0.8481, 6.89% OH, OH number of 227.3).

If one assumes that the secondary alcohols present in the non-esterifiable portion have the same average chain length as the esterifiable primary alcohols, it results that the non-esterifiable portion of Oxo alcohol consists of 56% secondary alcohols and 44% paraffins. Therefore the unfractionated charge consists of around 86% primary, 7% secondary alcohol and 5% paraffins. From this the conclusion is to be drawn that the unused excess of 10% alcohol, calculated on hydroxyl number, is by all means necessary, since with the found content of 7% of secondary alcohol performance is actually with an excess of only 3% of primary alcohol.

The monoester obtained is subsequently again saponified, the resulting alcohol purified by steam distillation, and esterified to Palatinol with phthalic anhydride. (Here only the theoretically necessary amount of alcohol is introduced, referred to OH:11.75, corresponding to a hydroxyl number of 386.7 and an apparent molecular weight of 144.8).

#### Physical Properties of the Ester

Specific Gravity	0.9940
Neutralization Number	0.028
Saponification Number	276.5
Hydroxyl Number	0
Viscosity	119.7 centipoises

There is calculated for the Palatinol a molecular weight of 415.4 from the saponification number, and one of 137.5 for the esterifiable portion of the alcohol, which corresponds to an average chain length of 08.5.

Translated by C. C. Miller, February 21, 1947  
Requested by Information Division  
Information Division Translation T47-16  
Typed 2/21/47

/s/ Petzold

"Palatinol from Oxo alcohol"  
I.G. Farbenindustrie A.G.  
Werk Offenbach am Main  
Betriebs-Abteilung  
June 29, 1944  
3 pages, no illust.

of the product; this clearing may be carried as far as desired, depending on the amount of adsorbing agent used and on the other experimental conditions applied. Furthermore, this process leads to extensive removal of the iron contained in the products. This is very surprising because a large part of the iron is present in the form of organic compounds which are usually hard to remove or to clear.

As diluents, hydrocarbons of varying constitution may be considered, especially aliphatic and alicyclic ones; among the latter, methylcyclohexane, isopropyl cyclopentane and alkyl substituted decahydronaphthalene may be given as examples.

In general, completely saturated hydrocarbons are to be preferred to those of the same structure but containing one double bond. For instance, a hexane is preferable to a hexylene, a cyclohexane better than a cyclohexene. As diluents or solvents, individual compounds or mixtures may be used; among the latter are especially those products which are obtained on industrial scale, especially fuels prepared by high-pressure hydrogenation of brown coal tar, brown coal, coal, etc., or also the fuel fractions obtained by the reduction of carbon monoxide with hydrogen, such as for instance the so-called Kogasin I; and also other industrial products such as fuel obtained from the brown coal low temperature carbonization process\*, either in crude form or after a further treatment such as for instance hydrogenation.

As adsorbents, various large-surface substances may be used; as examples, we may cite: natural or artificial bleaching earths<sup>1</sup> such as Fuller's earth, Floridine, Terrana, etc.; further-

---

\*Schwelbenzin (Transl.)

more, other adsorbing substances such as active coal, solid gels of silicic acid, aluminum hydroxide and others. Mixtures of these adsorbents may also be used. Furthermore, if one operates in several stages, different adsorbents may be used for each stage, e.g. active charcoal in the first stage and a bleaching earth in the subsequent stage. The temperature applied for the clearing process can vary within wide limits. Liquid products may be purified at ordinary temperature. Others, which are of high viscosity or solid, and which only at higher temperatures have a sufficient solubility in the above mentioned hydrocarbons, may be treated at temperatures of 50°, 80°, 100° and higher.

The adsorption equilibrium will be reached more rapidly if the liquid containing the substances to be purified is continually agitated. If the adsorbing agent is in form of a powder, this can be accomplished by stirring; with solid adsorbents, the same effect can be reached by continually pouring the liquid over the chunks of adsorbent, e.g. by fixing the latter in a tower and then pumping the liquid over it.

The amount of solvent which contains hydrocarbon depends on its nature as well as on the composition of the solute, and furthermore on the temperature applied. In general, it may be within very wide limits; it may be smaller, equal to, or considerably greater than the substance to be cleared.

Similarly, the amount of adsorbent depends on the other conditions and may be varied within a wide range. In general, it amounts to only a fraction (e.g. from 1%-30%) of the weight of the total amount of substance to be cleared. The separation

of the adsorbing agent from the liquid may be carried out by any one of the known methods, such as filtration, sedimentation, centrifugation and similar procedures. The adsorbent may be freed from the liquid parts which stick to it, by thorough washing.

The procedure described is especially suitable for the breakdown of those synthesis products or of their higher boiling components, which contain, besides hydrocarbons, also a considerable amount of oxygenated organic compounds; especially alcohols and other products which are formed during the conversion of carbon monoxide with hydrogen in the presence of iron catalysts at medium pressures (ab. 8-25 atm.) and at temperatures below 250° which are definitely below the level at which mainly or exclusively hydrocarbons are formed. But also those synthesis products which consist mainly or exclusively of hydrocarbons, may be cleared by the procedure described above.

After use, the color of the adsorbent almost always ranges from dark brown to a deep black, and the adsorbent itself is no longer suitable for further use. It was found that the adsorbent may be regenerated by a very easy method which consists in treating it with organic, oxygenated, halogenated or cyclic solvents; this treatment may be followed by a further treatment with acids. By means of the solvent, the adsorbent is extensively cleared, should it have been of light color already before use as adsorbent. By treatment with acid, which may be carried out in aqueous, alcoholic or also other solution, the regeneration of the adsorber is still increased. For this purpose,

dilute hydrochloric acid, sulfuric acid or similar acids may be used. The adsorbent treated with acid is then centrifuged, thoroughly rinsed with water and treated, for the removal of the latter, with an organic solvent; thus after desiccation or removal of the last named solvent by the above-mentioned hydrocarbon-containing solvent, they may again be used as solvents.

The oxygen-containing solvents which may be considered for our purposes are: low alcohols, such as ethanol and propanol; esters, such as acetic acid ethyl esters or butyl acetate, propyl formate or other formic acid esters of the low molecular alcohols; ketones, such as acetone and methyl ethyl ketone, ethers, such as diethyl ether, dipropyl ether, dibutyl ether and others. These substances may be used individually or in mixtures. Examples of halogen-containing solvents are: chlorine compounds such as trichloro ethylene, chloroform, carbon tetrachloride and also the compounds of other halogens, such as dibromo propane. As cyclic compounds are of importance: decahydronaphthalene, tetrahydronaphthalene and, above all, the strongly unsaturated hydrocarbons such as benzene, toluene, xylene, etc. The treatment of the adsorbing agents with these solvents occurs as a rule at their boiling temperatures which, depending on whether higher or lower pressures are used, will be correspondingly lower or higher. The best operating temperature is between 50 and 150°. The period of the treatment, which depends on the nature of the substances which are to be adsorbed, amounts usually to two hours or more; in some cases, the treatment extends to 8-12 hours; on the other hand, it may also be less than two hours.

The clearing action described in the above paragraphs is sufficient for using the various products as waxes for the coating of linoleum, furniture, leather, etc., and for similar purposes. On the other hand, the products cannot be used as cream base\* since

---

\* Salbenzusatz (Transl.)

the degree of clearing is not yet sufficient for pharmaceutical or cosmetic purposes. Furthermore, small amounts of unknown odorants are still present which have a disturbing effect.

It was now found that still further clearing may be achieved very advantageously by hydrogenation. This hydrogenation runs much better after the adsorptive process than without it. In the latter case, much sharper hydrogenation conditions must be maintained in order to achieve total discoloration; when this is the case, the high molecular compounds split partly into lower molecular compounds and even gaseous hydrocarbons are formed. If high boiling residues are hydrogenated without previous bleaching, a faintly grey-green color tone remains whereas pre-bleached products become white after hydrogenation. If alcohols, esters and similar compounds are contained in the products, these compounds, when subjected to hydrogenation, are converted to a great extent into hydrocarbons if they are not pre-bleached; this decreases the value of the reaction products greatly. If, however, one hydrogenates after the above-described adsorptive treatment, substantially milder conditions will suffice. One may thereby conserve the alcohols almost completely and, if one wishes, one may split the esters present in the product into alcohols; thus, not only the color of the product may be changed, but it may also be considerably improved in its chemical composition. Furthermore, the adsorptive pretreatment of the synthesis products greatly lengthens the life of the hydrogenation catalyst.

The hydrogenation is carried out, depending on the effectiveness of the particular catalyst employed, at temperatures



varying between 200 and 400°C.; in general, however, the temperature is much lower, e.g. by about 30°, than the temperature required for the hydrogenation without previous adsorptive treatment of the products. It will be advantageous to work at higher pressure, such as 50 atmosphere or, better, even higher; especially favorable is a 200 atm. pressure. The treatment can be made in individual batches or in one batch, in the autoclave; or continuously in a high pressure reactor with heatable in and outlets through which trickle the products to be subjected to the hydrogenation. The contact time of the products in the hydrogenation reactor, i.e. the period of hydrogenation in the continuous operation, amounts to anywhere between 1/2-2 hours; the rate of throughput per hour is 0.5-2 space units of product per catalyst space unit.

As hydrogenation catalysts, the various compounds known to be efficient may be used; for instance copper chromite, copper barium chromite, cobalt, nickel, copper and similar metals; furthermore some sulfur containing compounds such as molybdenum sulfide, tungsten sulfide, zinc sulfide, iron sulfide, either singly or in mixtures; these sulfidic catalysts may also be treated with any one of the known activators such as alkalies, alkali sulfide, etc.

Example 1

A carefully purified water gas is converted at 25 atm. and 250°C. in the presence of a so-called fused iron catalyst. This catalyst is obtained by melting iron (in some cases activating compounds are added) in an oxygen stream and then reducing

the mixed iron oxide which is formed. The compound obtained is almost exclusively composed of saturated and unsaturated hydrocarbons; it is separated, by cooling, from the residual gas: an oily layer separates from the aqueous layer. By further cooling, the oily layer congeals still more, and a dirty brown paste-like mass is obtained which will now be subjected to distillation. The residue boiling above 350° is a deep dark brown, almost black mass, the consistency of which is about equal to that of bee's wax. Twenty liters of this residue are now dissolved in 35 liters triisobutane and the solution is then strongly agitated, at 105°, with 4 kg. of porous "tonsil"\*, for a period of three hours. The gel is then filtered at higher temperature (it is very easily separated from the liquid), and the filtrate is further freed from the last remnants of solvent in vacuo. The residual high boiling mass is found to be extensively cleared when compared to the above mentioned distillation residue; its color is a light white-yellow. The iron content, initially 0.12%, has been decreased to 0.01%.

If various different solvents are used instead of triisobutane, such as triisobutylene, decahydronaphthalene and xylene, the color ranges and degrees of clearing shown in the table below are obtained. The degree of clearing obtained with triisobutane is taken as 10.

Solvent	Color Range	Degree of Clearing
Triisobutylene	Yellow	7
Decahydronaphthalene	Light yellow	8
Xylene	Brown	2 to 3

\*Tonsil = a word probably compounded from "Tonerde" (clay) and "Silica". (Transl.)

The clearing effect, accordingly, is more pronounced, the more the solvent resembles in its characteristics to a saturated aliphatic hydrocarbon.

If one works at the same temperature without solvent and with the same amount of adsorbent clay, the mass is cleared to an extent corresponding, in the scale established above, to about 6. However, in this case the high boiling residue is very difficult to separate from the adsorbent, so that the filtration is extremely slow and the adsorbent, even after the filtration, still contains large amounts of the high boiling residue.

The used adsorbent is extracted successively, for 24 hours each time, with the following solvents: 1) decahydronaphthalene; 2) acetone. With decahydronaphthalene, 1.18 kg. of deep black mass was removed from the gel; with acetone, 0.3 kg. After this treatment, the adsorbent gel can then be re-used for the clearing of synthesis products; it still has about 40% of its original clearing capacity.

If the adsorbent is further boiled with dilute hydrochloric acid, and then washed with water and methanol, it regains 80% of its original activity.

#### Example 2

The conversion of carbon monoxide with hydrogen, described in Example 1 above, is carried out at about 195°; thereby, a product with an average alcohol content of 50% is obtained. Again, this product is distilled and the residue (boiling above 400°) is dissolved in decahydronaphthalene; it is then bleached with silica gel (?) and subjected to hydrogenation at 280° in the

presence of 10% (by wt.) of a copper/barium chromite-containing catalyst for two hours; the hydrogen pressure is kept at 200 atm. Thereby, the color changes to a pure white. The alcohol content (OH No. = 16) is increased, due apparently to ester split (Ester No. = 38). Even after having been used for 5 times in succession, the catalyst showed no appreciable activity decrease.

If, on the other hand, the synthesis product is subjected to hydrogenation without previous adsorptive treatment, the temperature must be maintained at 310°C., all other conditions remaining the same; the hydrogenation product still has a grey green color tone and contains almost no alcohols or other oxygenated compounds. Already after a single conversion, the catalyst has lost so much of its activity that it must be subjected to a regeneration process.

#### Patent Claims

1. Process for the clearing of colored, high boiling component-containing products of the carbon monoxide/hydrogen conversion; the process is characterised by the treatment of the products when diluted with solvents which consist mainly of saturated or not too extensively unsaturated aliphatic or cyclic hydrocarbons.
2. Process for the further clearing of the products after treatment according to Claim 1 above, by treatment with hydrogen in the presence of catalysts.
3. Process for the clearing of synthesis products after Claim 1, characterised by the fact that the used adsorbents may

be regenerated by treatment with organic oxygenated, halogenated or cyclic solvents and, in certain cases, by subsequent treatment with acids; the regenerated adsorbent is then used again for the same purposes.

TOM Reel 15 pp 1566-1617

Bag 3043 Target 30/4.02

Page 1566

Rough calculation concerning the yield of unsaturated hydrocarbons which can be recovered from the tunnel-kilns-carbonization gases

According to information obtained from the Balt-oil-Company the permanent gases from plant #1 contain the following unsaturated hydrocarbons: (Analysis was performed in London)

Included the topping gases:

22 cbm per metric ton of shale  
Ethylene : 3.5%  
Propylene : 6.0%  
Butylene : 4.3%

Without the topping gases

20.7 cbm per metric ton of shale  
Ethylene : 3.9%  
Propylene : 4.3%  
Butylene : 3.1%

The volume of the topping gases amounts to 6% of the permanent gases and equals approx. 7-8 cbm per metric ton of crude oil.

The following amounts of unsaturated hydrocarbons are obtained from 1 metric ton of shale:

Ethylene 0.66 (0.77) cbm  
Propylene 0.95 (1.32) "  
Butylene 0.68 (0.95) "

The figures in parentheses represent the total volumes consisting of carbonization and topping gases.

Assuming an average output of oil shale of 1675 metr. tons per day plant I. and 710 metr. tons per day plant III, (tunnel kilns) the following volumes can be expected:

Plant I

Ethylene : 1100 (1300) cbm = 1375 (1625) kg  
Propylene 1600 (2200) " = 3000 (4150) "  
Butylene 1150 (1600) " = 2850 (4000) "

Plant III

Ethylene 470 (550) cbm = 550 (700) kg  
Propylene 675 (950) " = 1220 (1750) "  
Butylene 480 (675) " = 1200 (1700) "

Berlin, April 28, 1942

Signature

Extract from the proceedings of a meeting held at the office of  
The Continental Oil Company April 10, 1942

**Subject:** Oil-shale carbonization in Estonia

For the time being 4 plants are in operation, 2 of which are supposed to be enlarged while the remaining 2 will be shut down in the future. In addition the construction of a large carbonization plant at Tevel is under consideration. Finally, included the plants Kohtlor, Kivioli, three plants will be available for the recovery of shale-oil.

Oil-Production:

Assuming an oil yield of 20% and after the completed repair of the damaged plants the following quantities of shale-oil shall be recovered:

from the end of 1942	200,000 metric tons per year
1943	370,000 " " " "
final production 1944	560,000 - 600,000 " " "

The planned Tevel plant is supposed to produce 210,000 metric tons of oil per year.

The mining, crushing and screening costs per 1 metric ton of shale oil RM 3-4. (Costs are much too high! Translator). The fuel oil is sold for RM 51.- per metric ton of shale.

The oil-shale resources are estimated as high as 5,000,000,000 metric tons with a recoverable oil yield of 1,000,000,000 metric tons.

The Russian carbonization plants which are situated just on the other side of the Estonian border are supposed not to be enlarged due to the high mining costs.

Types of furnaces available for the carbonization:

(1) The Pintsch-Producer yields a little less oil than the tunnel kiln but very large gas volumes (fuel gases). The size of the shale should not exceed 25 mm.

(2) The Tunnel kiln is able to carbonize shale pieces as small as 10 mm (65% of the total mined shale). Because only small gas volumes are liberated an additional heating source must be employed. If the stokers are operated with fine shale, there arise many difficulties inside the flues due to formation of deposits of flue ashes. It is therefore contemplated to combine the Pintsch-producers with the tunnel kilns in such a manner that the liberated gases which leave the Pintsch producer are utilized as additional fuel for the tunnel - kilns. The oil which is recovered by the tunnel-process is supposed to be superior to that of the Pintsch producers.

Recovered Products:

Gasoline	12%
Tractor-fuel	4"
Bunker-fuel	27"
Bitumen	17.5"
Losses	2.5"

Hitherto only 10% gasoline were topped and a small amount of bitumen was produced, leaving a fuel oil with a high asphalt content for sale.

The recovered gasoline is said to contain 62% unsaturated hydrocarbons and to show a good anti-knock value. The diesel-oil fraction contains approx. 50% unsaturated hydrocarbons; blended with other oils it is used as diesel-fuel in Estonia. A contract was concluded with the navy which promised to buy 200,000 to 250,000 tons of bunker-oil per year. The bitumen can be used as road building material or after carbonization

as raw material for the fabrication of electrodes (aluminum industry). The gases which are liberated during the carbonization shall serve as an additional source for heating purposes of the tunnel kilns.

According to Ruetgers the shale oil is an excellent solvent for coal-tar-hydrocarbons.

By-products:

The total oil contains 10% phenolic constituents, the middle oil fraction approximately 20%. Hitherto phenols were recovered during the refining of the gasoline.

No figures were available concerning the quantity and the phenol-content of the waste liquors.

Acetone was recovered from the waste liquors, information about the quantity and quality of the recovered acetone was not available.

Composition of the liberated gases (Type of furnace unknown, presumably tunnel-kiln 22-25 cbm per ton of shale)

H <sub>2</sub> S	7.4%	vol.	} permanent gases
Mercaptan	1.5%	"	
CO <sub>2</sub>	18.0%	"	
CO	6.0%	"	
H <sub>2</sub>	6.1%	"	
C <sub>2</sub> H <sub>4</sub>	3.5%	"	
C <sub>2</sub> H <sub>6</sub>	6.0%	"	
C <sub>3</sub> H <sub>8</sub>	4.3%	"	
CH <sub>4</sub>	21.1%	"	
C <sub>2</sub> H <sub>6</sub>	11.0%	"	
C <sub>3</sub> H <sub>8</sub>	6.3%	"	
C <sub>4</sub> H <sub>10</sub>	3.0%	"	
N <sub>2</sub>	5.7%	"	
O <sub>2</sub>	0.1%	"	

The thermal value of the gas after extraction of the hydrocarbons (gasoline polymerization !) is negligible.

Sulfur content of the total oil: 1%